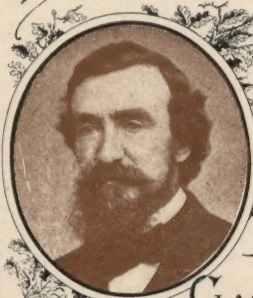


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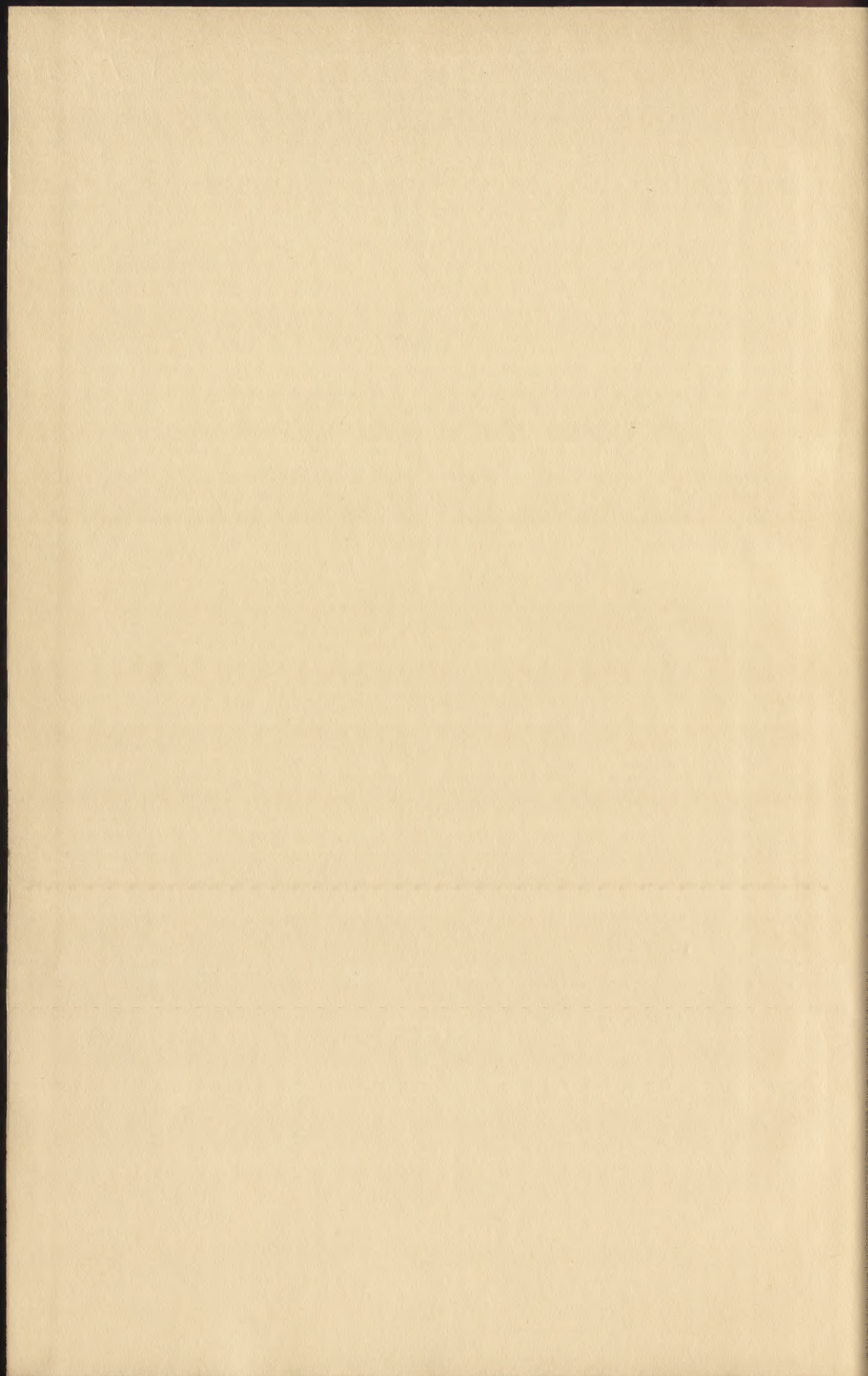
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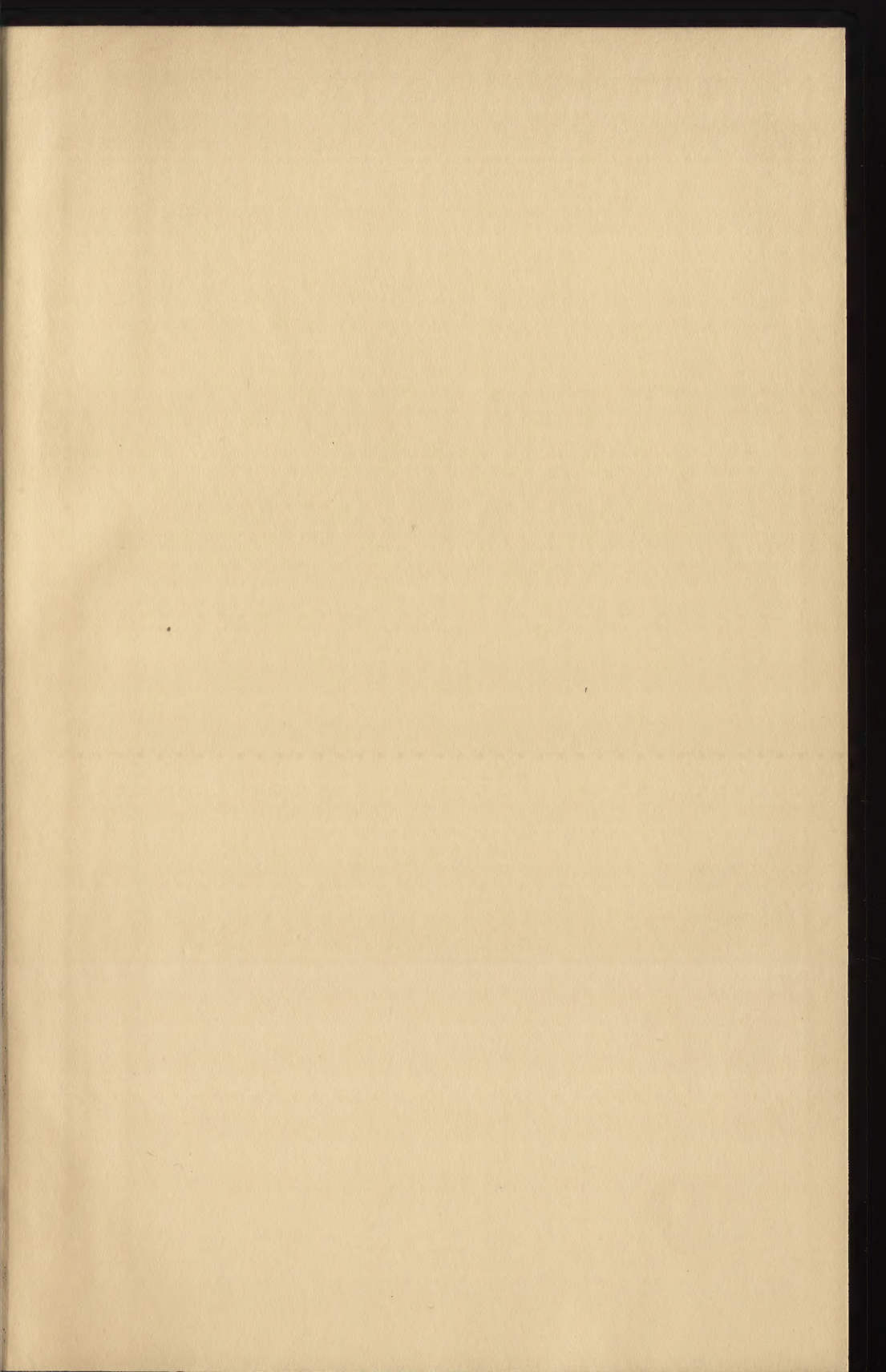
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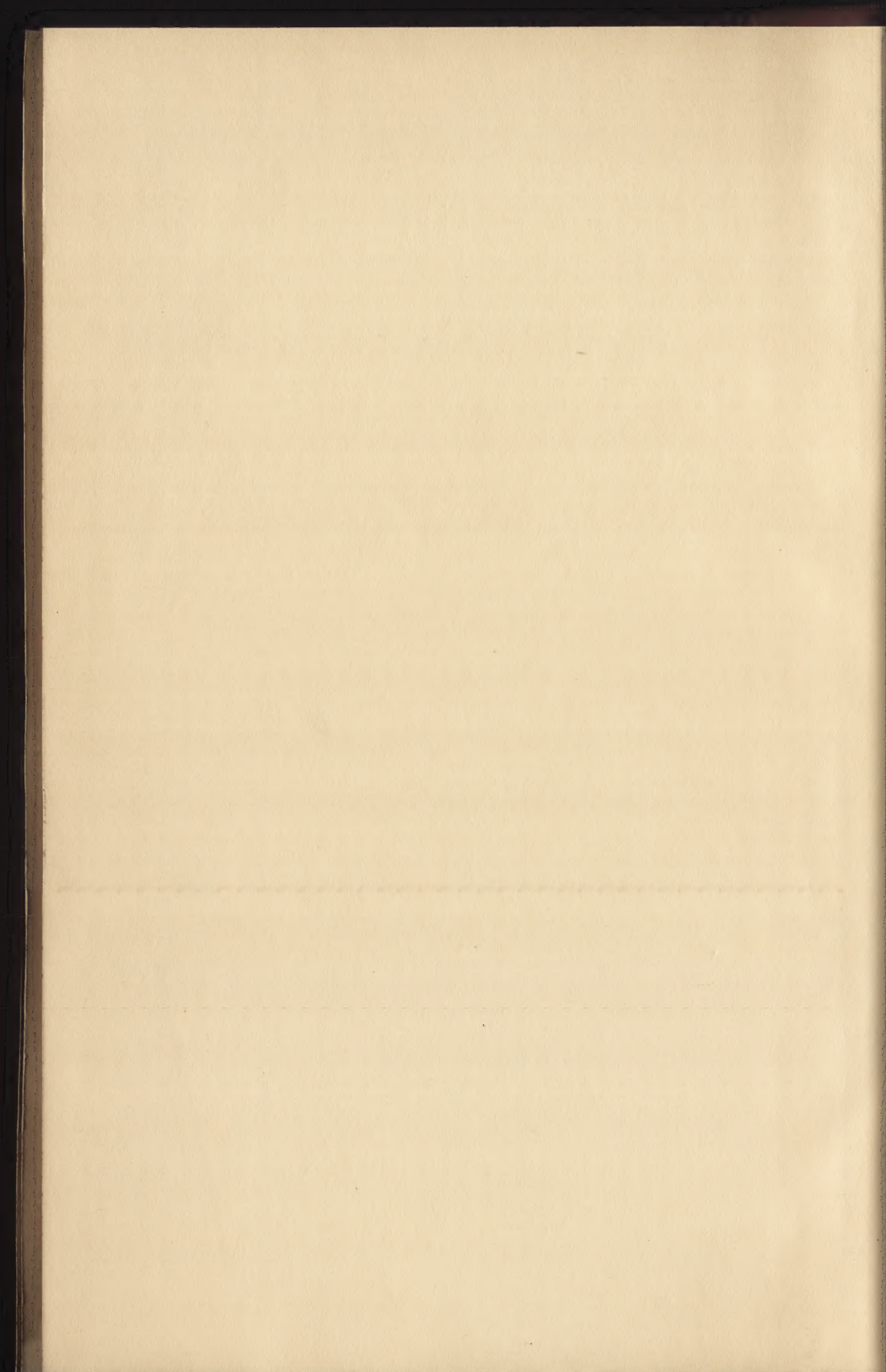
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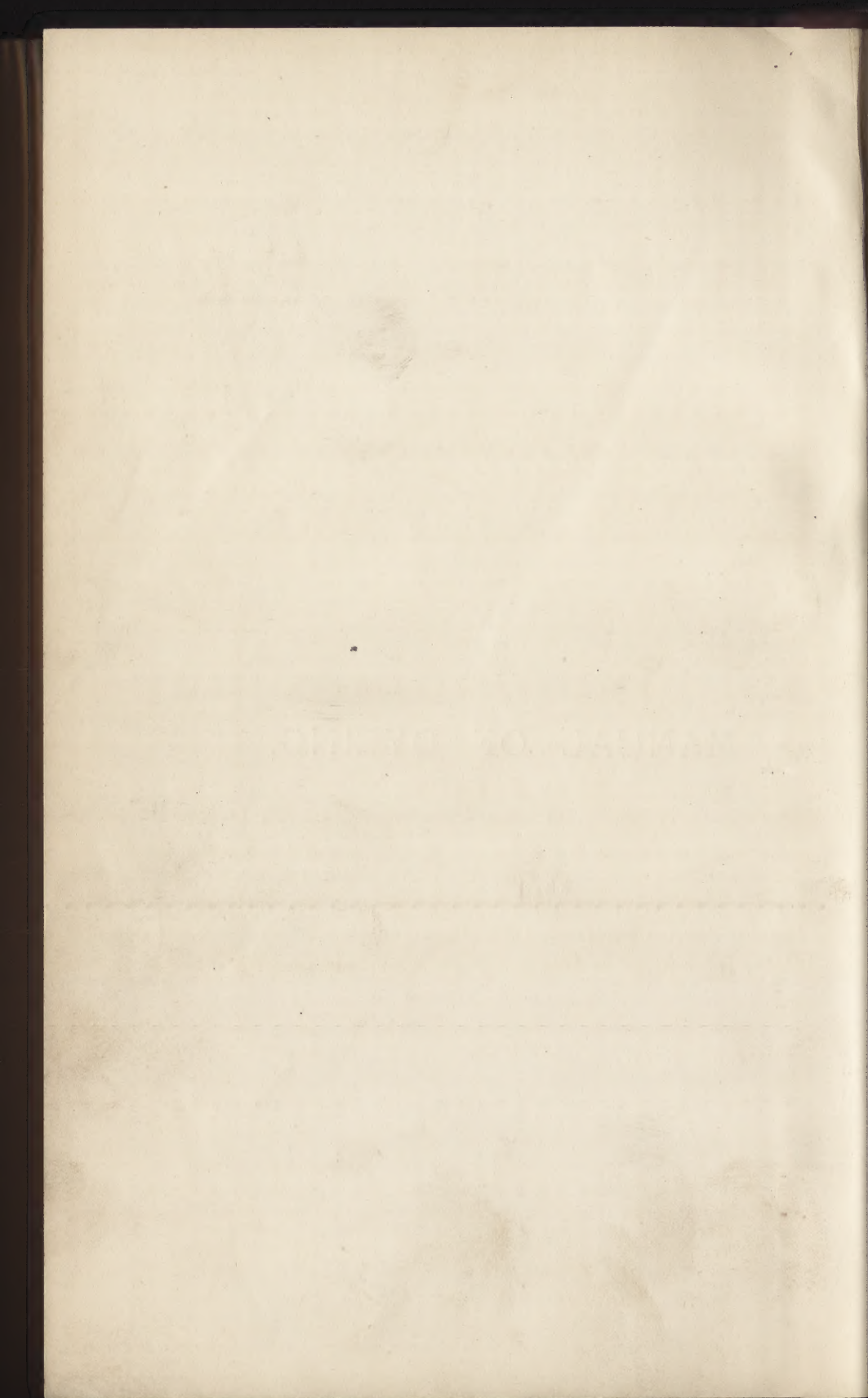






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A
MANUAL OF DYEING.



A

MANUAL OF DYEING:

FOR THE USE OF PRACTICAL DYERS, MANUFACTURERS,
STUDENTS, AND ALL INTERESTED IN THE
ART OF DYEING.

BY

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WITH NUMEROUS ILLUSTRATIONS AND SPECIMENS OF DYED FABRICS.

VOL. I.

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MANUAL OF INQUIRY

THE FOLLOWING INFORMATION IS FOR THE
USE OF THE INQUIRY OFFICER
ONLY.

INVESTIGATION OF THE CASE

REPORTED BY THE
INQUIRY OFFICER

INVESTIGATION OF THE CASE

PREFACE.

THE preparation of this Volume was originally undertaken at the request of the Publishers, with the view of producing a work based on lines similar to those pursued in the late Mr. James Napier's *Manual of Dyeing and Dyeing Receipts*. Dyeing, however, like every other art, is progressive, and the main point of contact between the present book and Mr. Napier's Treatise—widely-known and highly appreciated as it was in its day—is that we, like him, have based our work on the study of First Principles, and have endeavoured so to combine Theory and Practice as to lead the Reader to think out for himself the new possibilities which must necessarily present themselves in an ever-widening field.

In carrying out this object, it has been our endeavour to lay down the leading principles involved in Dyeing and accessory operations, together with such exact information on the Technology of the fibres, mordants, colouring-matters, &c., as was obtainable. All the most important English and foreign standard works and Journals bearing on the subject of Dyeing have been consulted. In many instances we have thought it advisable to make references to original publications, and in some cases to English translations or abstracts of articles taken from foreign journals.

Our aim has, therefore, been to produce a work which would serve more as a book of reference or *vade-mecum* to the educated dyer, than as a mere "cookery-book," containing "rule-of-thumb" recipes, more or less reliable. But although a knowledge of analytical chemistry is essential to any one wishing to make use of the chapter dealing with the Analysis of Substances employed in Bleaching and Dyeing, we have endeavoured to put the information contained in the rest of the work in such a form that it will also be intelligible to dyers who have not had the advantage of a scientific training.

We take this opportunity of acknowledging our indebtedness to Drs. Schultz and Julius for permission to make use of their excellent

Tables in compiling the chapter on Artificial Colouring-matters, as well as to the principal Colour Manufacturers for information on their specialities, and to those Engineers whose names are mentioned in the text as having supplied us with drawings and descriptions of machinery.

Our obligations are also due to Messrs. Edward Ripley & Son, of Bowling Dye Works, Bradford, and to Messrs. James Sharp & Son, of Low Moor, near Bradford, who have dyed the patterns on wool and cotton respectively in the accompanying Volume.

THE AUTHORS.

March, 1893.

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ABBREVIATIONS (PART VII).

B. A. S. F.	=	Badische Anilin- and Soda-Fabrik, Ludwigshafen-on-Rhine.
Bayer	=	Farbenfabriken, vorm. Fr. Bayer & Co., Elberfeld.
Berlin	=	Actien Gesellschaft für Anilin-Fabrikation, Berlin.
Bindschedler	=	Society of Chemical Industry (late Bindschedler & Busch), Basle.
Br., S. & S.	=	Brooke, Simpson, & Spiller, Ltd., London.
Cassella	=	Leopold Cassella & Co., Frankfort-on-Maine.
Clayton	=	The Clayton Aniline Co., Manchester.
Dahl	=	Dahl & Co., Barmen.
Durand	=	Durand, Huguenin & Co., Basle.
Fischesser	=	Alfred Fischesser & Co., Mulhouse.
Geigy	=	J. R. Geigy, Basle.
Holliday	=	Read Holliday & Sons, Ltd., Huddersfield.
Kalle	=	Kalle & Co., Biebrich-on-Rhine.
Kern	=	Kern & Sandoz, Basle.
Leonhardt	=	A. Leonhardt & Co., Mülheim in Hessen.
Levinstein,	=	I. Levinstein & Co., Ltd., Manchester.
M. L. B.	=	Farbwerke, vorm. Meister, Lucius & Bruning, Hoechst-on-Maine.
Monnet	=	Gillard, P. Monnet & Cartier, Lyons.
Oehler	=	K. Oehler, Offenbach-on-Maine.
Poirrier	=	Société Anonyme des Matières Colorantes (A. Poirrier & G. Dalsace), Paris.
Schoellkopf	=	The Schoellkopf Aniline and Chemical Co., Buffalo.
Thann	=	Fabriques de Produits Chimiques de Thann et de Mulhouse.

E R R A T A.

Page 23, line 8 from top, insert "unripe" before "cotton."

„ 37, „ 8 „ top, read "15.43" instead of "18.25," and insert "being equivalent to a *regain* of 18.25 per cent." after "moisture."

„ 80, „ 1 „ bottom, read "Berthollet" instead of "Berthellot."

„ 110, „ 24 „ top, read "permanganate" „ "manganate."

„ 150, „ 17 „ top, read " -8°C " instead of " 8°C ."

„ 170, „ 1 „ „ read formula: $\text{CO} \left\{ \begin{array}{l} \text{C}_6\text{H}(\text{OH})_3 \\ \text{C}_6(\text{OH})_3\text{CO}_2\text{H} \end{array} \right\} + \text{H}_2\text{O}.$

„ 296, „ 13 „ „ read "plumbites" instead of "plumbates."

„ 301, „ 1 „ bottom, read formula:—"(SbO) $\text{K C}_4\text{H}_4\text{O}_6 + \frac{1}{2}\text{H}_2\text{O}.$ "

„ 446, lines 7 and 14 from top, read "diamine blue-black E" instead of "diamine black-blue E."

„ 560, line 12 from top, read "alum" instead of "acetic acid."

„ 634, „ 20 „ „ read "analogous to" instead of "isomeric with."

„ 657, „ 9 „ „ read formula: $\text{N} \begin{cases} \text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2 \\ \text{C}_{10}\text{H}_6(\text{OH}) \\ \text{H} \end{cases}$

„ 744, „ 5 „ „ read "cork" instead of "cock."

„ 831, „ 10 „ „ read "formed" instead of "found."

A MANUAL OF DYEING.

PART I.

INTRODUCTION; THEORY OF DYEING.

IN its broadest sense, *dyeing* is the operation or series of operations by means of which uniform colour, of a more or less permanent character, is produced on, or in the substance of, objects. The term *tinting* is literally the same as dyeing, but is in its meaning only applied to the production of very light or delicate shades. *Staining* has a similar meaning, but the use of the term is almost entirely restricted to the production of coloured paper. In *printing*, the colour is applied to portions only of the material, and in such a manner as to produce a definite pattern.

The dyeing of textiles, either in the woven fabric or in the intermediate stages of manufacture, by far exceeds in importance the dyeing of other objects, such as leather, feathers, straw, horn, ivory, bone, wood, &c.; the former subject only will be dealt with in this work. But even if the scope of the work be restricted to this industry alone, it would be impossible to go into the details of every speciality. Indeed this is not its object, the main aim being to lay down broad principles, and to show how science, especially Chemistry, underlies most operations in dyeing, and may be usefully applied in detecting the origin of faults, in improving existing methods, or in working out new methods or effects. That a knowledge of chemistry is most useful to the dyer will scarcely be doubted; but the smaller his knowledge, the more circumspect should he be in making use of it. Chemistry has done a great deal towards the furtherance of the dyeing industry. During the last decade it has almost revolutionised certain portions of it, and it may be safely predicted that in the near future it will do much more than has been the case in the past.

The large number of *dyes* or *colouring matters* which are at the disposal of the dyer are principally of organic origin; some few are also derived from the mineral kingdom. The oldest classification of

these various substances is that of Bancroft, who divides them in his *Treatise on Permanent Colours* (published nearly 100 years ago) into *Substantive dyes* and *Adjective dyes*. According to this classification, we regard all dyes as Substantive which, like indigo extract, chrysophenin, benzopurpurin, &c., will dye the textile fibres directly. Adjective dyes will only dye material mordanted with a metallic salt or oxide, or with the addition of a metallic salt or oxide to the dye-bath—such are, for instance, logwood, alizarin, cochineal, fustic. In the pure state, the adjective dyes are generally but slightly coloured, and, when used alone in dyeing, they give rise to worthless results, which are not of a permanent character. But when used in conjunction with metallic mordants, such as the salts of iron, alumina, chromium, or tin, intensely coloured insoluble compounds—so called *lakes*—are produced in the substance of the fibre, which thus becomes dyed. Similar lakes can be produced without the presence of the fibre by adding the metallic salts either to the aqueous or to the slightly alkaline solution of the adjective colouring matter.

Bancroft's classification is still the one which is in most general use.

Nietzki's classification of the colouring matters into *direct dyes* and *mordant dyes* (that is, into such as will dye directly, and such as will only dye with the intervention of a mordant) is practically the same as Bancroft's.

Hummel* classifies the colouring matters as *monogenetic* and *polygenetic*. Monogenetic are such as are only capable of yielding one colour, whatever mordant may have been used on the material, either before or during the dyeing operation. Magenta, orchil, indigo, picric acid, methyl green, may serve as examples of this class. Polygenetic colours are such as are capable of producing totally different colours according to the mordant employed. Examples of this class are logwood, alizarin, fustic, and cochineal. The term *autogenetic* colours employed by Scheurer seems to be synonymous with Hummel's monogenetic class.

The direct dyes may be further classified as *direct dyes for cotton*, *direct dyes for wool and silk*: *acid dyes*, and *basic dyes*. The direct dyes for cotton will dye all textile fibres; the acid dyes are mostly only applicable to wool and silk; while the basic dyes have a direct affinity for wool and silk, but not for cotton. To be dyed with the basic dyes, the latter must be first mordanted with tannic acid or an oil mordant. In some cases, the mordant dyes may serve as fixing agents for the basic dyes on cotton. Thus, magenta is readily fixed on cotton which has been previously mordanted with alumina and dyed with alizarin.

Pigment colours are insoluble coloured substances like vermilion, ultramarine, or lamp black, which find little or no application in dyeing. They are used to some extent in calico-printing, and are fixed by means of albumen.

* *The Dyeing of Textile Fabrics*, p. 147.

The dyeing of textile fibres is almost invariably effected by immersing the material to be dyed in the solution of the dye in cold or hot water, and either keeping it moved in the dye solution or causing the latter to circulate through the material until the desired shade is obtained. In rare cases other solvents, such as benzine or alcohol, are employed in place of water. In any case the solvent simply acts as a distributing agent for the dye, [causing it to permeate more or less uniformly every part of the material. Exceptions are found to this in the case of *spray dyeing*, in which a fine spray of the dissolved dyestuff is blown on to the piece, and in dyeing one face only of the cloth by printing it with a thickened colour in a printing machine.

Dyeing is effected in *neutral*, *acid*, or *alkaline* solution, according to the material to be dyed and the dyestuff employed. Cotton is generally dyed, neutral or alkaline, not often in an acid bath. Wool is rarely dyed in an alkaline bath, but generally either acid or neutral. Worsteds dyed in an acid bath are said to finish better than when dyed neutral or alkaline. Silk is generally dyed in boiled-off liquor, *i.e.*, in an alkaline bath. In the black-dyeing of silk with logwood the bath is usually rendered alkaline by the addition [of soap. Many colours are only applicable to silk in an acid bath, and for these an acidulated bath of boiled-off liquor is employed.

The object of *mordanting*, an operation which, as a rule, precedes the dyeing, is to fix on the material to be dyed a *mordant*, generally a metallic hydrate or basic salt which is capable of forming a colour-lake with an adjective colouring matter. In mordanting wool and silk, practically the same operations are employed as in dyeing. In the mordanting of cotton, an additional operation, *viz.*, that of *ageing*, is frequently employed, especially for piece goods. The prime object of ageing is to cause the mordant (*e.g.*, basic sulphate or acetate of alumina), which the material retains by capillary attraction, to decompose evenly on and in the fibres. Sometimes, as is for instance the case with ferrous acetate, a simultaneous oxidation takes place. Ageing was done formerly (and is still done to a great extent at the present time) by suspending the material in ageing rooms, in which the temperature and degree of moisture of the atmosphere are kept as constant as possible in order to allow of a gradual and even deposition of the mordant on the fibre. The operation usually requires two or three days. Latterly the so-called *ageing machine* (see *Aniline black*), in which the pieces impregnated with the mordant solution are passed at full breadth through a chamber filled with steam, have to a large extent superseded the old ageing process. The process of ageing is also applied in the production of certain colours (*e.g.*, aniline black) on cotton. In this and similar cases the ageing effects an even oxidation of the colouring matter throughout the mass of the material.

If the dyed material still containing the hot dye-liquor is allowed to lie in heaps, it is often noticed that the colour is thereby considerably deepened. Whether this is due to a process of oxidation, or to what one might term an after-dyeing, is not certain. Advantage is sometimes taken of this in "smothering" the goods after dyeing, as is, for instance, frequently done with direct blacks produced with logwood and copper on cotton.

A similar after-effect is sometimes made use of in the mordanting of silk or cotton. The material, after having been thoroughly impregnated with the mordant solution, is evenly wrung out and left to lie in the wet state overnight. By contact with the fibre, the mordant is gradually decomposed, and its useful constituent fixes itself evenly on the fibre.

In the majority of cases the dyeing of the textile fibres is done above the ordinary temperature. For wool a boiling temperature is almost invariably employed; in the cold most colouring matters appear to have very little affinity for this fibre. Tannin-mordanted cotton may be dyed cold with the basic dyes, but in the majority of other cases the temperature of the dye-bath is maintained near the boiling point. High temperatures are not often employed in silk dyeing. Most colours are dyed on silk in a lukewarm bath.

In cotton dyeing, the amount of water usually employed is 20 to 30 times the weight of the material. For the direct cotton colours, which do not exhaust well, it is advisable to use a more concentrated dye-liquor. In dyeing such colours as crocein scarlet the dye-liquor is padded into the pieces in a padding machine, and is taken of such a strength that a single passage produces the required shade. For wool dyeing the amount of water employed is 50 to 100 times the weight of the loose wool, yarn, or slubbing, but stronger solutions are frequently used for pieces. The reason why wool requires so much more water than cotton is that it is more bulky than the latter; but it exhausts the dye-bath better. In silk dyeing the amount of water used in the dye-bath is somewhat greater than what is used for cotton. In any case, the volume of water required will also depend to a great extent upon whether the material is in the loose, spun, or woven state, the former requiring most, the latter least liquid.

In the *application* of the *direct dyes* the methods employed call for no special comment. The material is simply immersed in the cold, warm, or boiling (generally the latter) dye solution, and moved there continuously or intermittently until the required shade is obtained. After dyeing, the goods are generally washed off with water; but, in many cases, an after-treatment is necessary either for the purpose of developing the colour, rendering it brighter or more permanent, or giving a particular feel or handle to the material. Thus, in the dyeing of alkali blues on wool or silk, it is necessary, in order to fully develop the colour, to pass the material after dyeing through a hot

bath of dilute sulphuric acid. Cotton material is frequently treated after dyeing with a weak soap solution or an emulsion of oil in soap in order, on the one hand, to give the material a better feel, and, on the other hand, to brighten the colour. The soap or oil emulsion is not washed out, and the material is dried at once. The oil remains in the material and enhances the brilliancy of the colour, just as a varnish improves the appearance of the grain of a wood, or as water brightens the colours in a stone or pebble. In place of soap or oil emulsion, a solution of Turkey-red oil is sometimes employed after dyeing with a similar object. Silk dyed in an alkaline bath is frequently passed through dilute tartaric, acetic, or sulphuric acid in order to give it the peculiar crackling feel known as "seroop."

In the *application* of the *mordant dyes*, three distinct methods are employed. That most generally adopted, which is known as the *mordanting and dyeing method*, is to dye the material which has been previously mordanted with the dyestuff, which may either be in solution (*e.g.*, logwood) or in a state of suspension (*e.g.*, alizarin). The method termed in wool dyeing, *stuffing and saddening*, consists in first boiling the material with the colouring matter, as is, for instance, the case in the production of the old dyewood browns with camwood, fustic, and logwood, and subsequently developing in the mordant solution (*e.g.*, chrome or copperas). This method is not so frequently employed at present in wool dyeing as formerly. The browns, which were the principal colours produced in this way, have been largely superseded in recent years by those produced from logwood, fustic, and coal-tar colours by mordanting and dyeing, which are preferred either for greater fastness or greater cheapness. In cotton dyeing, chiefly in piece dyeing, this method of treatment is still much employed in the production of browns, drabs, and nearly all so-called "mode colours;" but more especially in those shades in which catechu is employed as a constituent. In cotton dyeing the term "saddening" is used to designate the treatment in the decoction of the dyewoods, and not, as in wool dyeing, the development of the colour in the mordant solution. The development of the colour in the mordant solution is practically known as "copperasing" or "taking off." A third method, lastly, of employing the mordant dyes is the so-called single-bath process ("one dip" dyes). In both the preceding methods, the insoluble colour-lake is produced on or in the fibre, but in the single-bath process, the lake to be fixed on the fibre is rendered soluble in the dye-bath, and is taken up by the fibre like a direct dye, as is, for instance, the case in dyeing cochineal scarlet on wool.

Theory of Dyeing.—In the last century the interesting phenomena observed in dyeing had already attracted the attention of scientists, and numerous theories have been brought forward from time to time with the object of explaining these phenomena. The majority of the theories advanced either assume that dyeing is due to

a mechanical absorption of the particles of the colouring matter by the substance of the fibre (mechanical theory), or to a chemical combination of the colouring matter with the substance of, or some substance contained in, the fibre (chemical theory).

Hellot and Le Pileur d'Alpigny* in the last century were the first advocates of a strictly mechanical theory of dyeing. They assumed that all fibres are porous; that the pores of one fibre are of a different size to the pores of another fibre of different origin; and that the number of pores is greater in some cases than in others. Thus, wool was supposed to have the pores of greatest diameter, and in a given space the largest number of these, and silk those of least diameter. The pores are expanded by heat and certain chemical agents in such a way as to admit the particles of colouring matter, and then, being closed by cooling or astringents, were able to retain them securely. To explain why dyes would not enter into combination with all fibres equally, the theory of different-sized pores was invented, and then different sizes were attributed to the particles of colouring matters. They, of course, allowed (as do other advocates of a mechanical theory) the influence of mordants as forming insoluble lakes with the colouring matters.

Walter Crum, another staunch supporter of the mechanical theory, maintained that in order to be able to resist washing, the colour must be enclosed by the fibre as by a bag or fine network; the colouring matters must be in the cells or pores of the tissue. He considers that there can be no chemical combination with the fibre, for, to use his own words, "if we only consider that chemical attraction necessarily involves combination, atom to atom, and, consequently, disorganisation of all vegetable structure; that cotton wool may be dyed without injury to its fibre, and that the fibre remains entire, when by chemical means its colour has again been removed, we shall find that the union of cotton with its colouring matter must be accounted for otherwise than by chemical affinity." Crum admits a power of attraction on the part of the cotton fibre, and a capability of its withdrawing chemical or colouring substances from their solutions. But in this force he only recognises that same action which enables charcoal to absorb gases, and remove colouring matters, and some salts and metallic oxides from solutions.

More recently, the mechanical theory has found another prominent adherent in Müller-Jacobs, who, in his series of articles on "Membranous Diffusion in Dyeing" in the *Textile Colorist* for 1885,† bases all the phenomena as observed in dyeing on exosmose and endosmose.

Witt's theory, lastly,‡ forms as it were a bridge between the mechani-

* See Ch. O'Neill's *Chemistry of Calico Printing, Dyeing, and Bleaching*, p. 316.

† See also *Journ. Soc. Dyers & Col.*, 1885 and 1886.

‡ See *Journ. Soc. Dyers & Col.*, 1890, p. 173.

cal and chemical theories. He regards the fibres as solid solvents, which in dyeing extract the colouring matter from the aqueous solution of the dye-bath; just as, for instance, ether will extract or dissolve out resorcin from its aqueous solution if shaken with it. The degree to which the dye-bath will be exhausted will depend entirely upon the relative solubility of the colouring matter in the dye-bath (water), and in the substance of the fibre. In his excellent treatise on the matter, Witt gives numerous examples in illustration of the correctness of his theory. Unfortunately, however, these are only of a qualitative nature; it should not be difficult to test the correctness of the theory by quantitative work, although this would necessarily involve the expenditure of much time and trouble.

The chemical theory may be said to have more adherents than the mechanical theory. It is the one which has been accepted by most of the writers on dyeing; but, as O'Neill remarks (*l.c.*), as these writers are for the most part chemists, it is not, perhaps, wonderful that they should have adopted a chemical theory. In the last century already, Bergman and Macquer strongly opposed Hellot and Le Pileur d'Alpigny. Subsequently the chemical theory was supported by others, notably by Persoz.

It is, perhaps regrettable that during this long controversy the adherents of the one theory or the other have confined their observations almost entirely to one particular kind of fibre, and have extended their conclusions to dyeing generally. If there is, chemically, not as much difference between cotton and wool as there is, to use a popular expression, "between chalk and cheese," they at least differ from each other as much as a higher alcohol does, for instance, from albumen. Both substances—cellulose and keratine—happen to form fibres; but what holds good for one, must not necessarily also hold good for the other.

In their composition and their general behaviour towards chemical agents it has been seen that the animal fibres differ entirely from those of vegetable origin. While the latter are regarded as hydroxyl compounds, and can scarcely possess other than slightly acid properties, the animal fibres possess both acid and basic properties; to this fact no doubt is due their power of combining with a much larger range of colouring matters than is the case with the vegetable fibre.

The chemical theory is strongly supported by the following facts:—

1. The textile fibres possess either acid or acid and basic properties. This is proved in the first place by their well-known property of absorbing acids, alkalies, and certain salts from aqueous solution, and retaining them tenaciously.* A further proof, in the case of wool and silk at least, is furnished by the thermo-chemical researches of L. Vignon.†

* See Mills & Takamine, *Journ. Chem. Soc.*, March, 1883; also, Fürstenhagen & Appleyard, *Journ. Soc. Dyers and Col.*, 1888, p. 124.

† *Journ. Soc. Dyers and Col.*, 1890, pp. 86 and 120.

2. There is no colouring matter which does not possess either acid or basic properties.

In the dyeing of wool, for which fibre the largest number of colouring matters have a direct affinity, the following additional facts have been established :—

1. If wool is dyed in a solution of the hydrochloride of a basic coal-tar colour, the whole of the hydrochloric acid remains in the solution.*

2. Wool boiled in a colourless solution of rosaniline base is dyed as with magenta.

These simple facts point dead against the assumption of a mechanical theory as far as wool is concerned, and the same will be found to be the case with silk. According to the mechanical theory, wool dyed with magenta, for instance, would simply absorb the unchanged hydrochloride of the dyestuff, and thus assume the same colour in the solution of the dyestuff. But experiment has shown that this is not the case. It absorbs the colour base, which is, however, in itself colourless. Where then does the colour come from? We can come to no other logical conclusion than that the colour base has combined chemically with some constituent of the fibre to form a coloured salt. Against this it may be argued that the combination not taking place in molecular proportions, no chemical action can be assumed; we can dye wool with magenta from the faintest tint of pink to a maroon. This objection is easily met by assuming that what is taken up is in chemical combination with some insoluble constituent of the fibre, and is held by the rest of the transparent or translucent substance of the fibre in a state of *solid solution*. The combination may be stable, as is, for instance, the case with azocarmin; or unstable, as is the case with picric acid; and this constitutes the difference between fast and loose colours. But that in the dyeing of wool the laws which govern chemical combination are not totally disobeyed is shown in dyeing it with two similarly composed colouring matters like picric acid and naphthol yellow. Wool dyed under similar conditions with a large excess of each of these colouring matters showed that while of the former 13.3 per cent. were absorbed, 20.8 of the latter were taken up from the aqueous solution. The calculated chemical equivalent for the latter would be 20.6 per cent.†

The acid colouring matters behave in a different manner towards the wool fibre. Wool boiled in the neutral solution of an alkali salt of one of the acid dyes, takes up very little colour. But if sulphuric acid is added to the dye-bath, the absorption takes place rapidly, and in most cases the dye-bath is exhausted. In this case, no doubt, the free colour acid is liberated, and as this is in most cases an intensely

* *Journ. Soc. Dyers and Col.*, 1888, p. 72.

† *Journ. Soc. Dyers and Col.*, 1889, p. 74.

coloured compound, it might be argued that, with acid dyes at least, the dyeing is simply a mechanical absorption. But if wool is boiled with a small amount of sulphuric acid (say 5 per cent.) and then extracted again and again with boiling distilled water, until even the most delicate indicator fails to show the presence of free acid after an hour's boiling, it acquires the property of becoming dyed with the neutral solutions of the acid dyes in full, saturated colours. Although no attempts have hitherto been made to determine the amount of alkali left in solution, the case seems to be analogous to the dyeing of wool with the basic dyes.

Both wool and silk, when completely disintegrated by strong acids or alkali, yields products (lanuginic and sericinic acids respectively) which are soluble in water. Their aqueous solutions possess the peculiar property of forming insoluble lakes with the direct colours for wool and silk. Now, if a solution of albumen is boiled with a known quantity of the hydrochloride of a basic colouring matter, the colour is removed and the whole of the acid to which it was bound remains in solution, as is the case in wool dyeing. (Private communication from Prof. Liechti.) Here, then, there can be no doubt of a chemical combination having taken place, since the coagulated albumen has become dyed an intense shade of magenta. Is it not possible that lanuginic acid, which contains the same elements as the substance of the wool fibre, though in different proportion, should exist in the fibre in an insoluble state; and that the same applies to the sericinic acid obtained from silk?

In the dyeing of wool and silk, the above considerations seem to point to chemical and not mechanical action in dyeing.

With cotton and the other vegetable fibres, little exact or quantitative work has as yet been done, and the question as to whether here the dyeing is due to mechanical absorption or solution, or to chemical combination must still remain an open one. With the large numbers of direct cotton colours which are placed at our disposal, and which are continually increasing in number, the question becomes more and more important from a theoretical point of view. It is not probable that it will ever be solved by vague theoretical speculations based on one or two known facts. In all probability the solution of the question will require much laborious work, including many quantitative determinations.

If it could be shown that oxycellulose, which has a direct affinity for the basic colours, behaves like wool and silk in assimilating or combining with the basic constituent and leaving all the acid in solution, this would, no doubt, form an important step towards the establishment of a chemical theory for cotton dyeing.

The *mordanting* of wool and silk appears to be analogous to the dyeing of these fibres, and to depend upon their acid and basic properties. Thus, wool boiled with a solution of aluminium sulphate

fixes both the acid and the basic constituent of the salt; but, being possessed of more pronounced acid than basic properties, it absorbs the basic constituent more energetically than the acid one, and some free acid is left in the solution. By subsequent treatment with boiling water, more acid is extracted, and the alumina becomes more firmly combined with the substance of the fibre. It is noteworthy that only such salts which contain the acid and basic constituents in a comparatively loose state of combination are absorbed by the wool fibre. Thus, whereas the sulphates of aluminium, iron, chromium, and copper are readily taken up from the boiling solution by the wool fibre, sodium sulphate or sodium chloride are not taken up at all.

PART II.

CHEMICAL TECHNOLOGY OF THE TEXTILE FIBRES.

A KNOWLEDGE of the chemical and physical properties of the textile fibres, and of their behaviour towards the various substances which they are likely to come in contact with, either during the process of manufacture or afterwards, as well as their behaviour under varying conditions of moisture and temperature, is of the greatest importance both in dyeing and finishing. The two most important things which the dyer has to deal with are, in the first place, the material to be dyed; and, secondly, the materials or substances used in producing the desired colours and effects. Unfortunately, the exact study of the former subject (the textile fibres), from a chemical and physical point of view, has been somewhat neglected, and there are at present still many points on which more extensive and more exact information would be desirable. Chemists have hitherto usually turned their attention to more straightforward, and perhaps more remunerative, work; but, at present, increased signs of activity have shown themselves in this important field of research; and it is to be hoped that this will be rewarded by results valuable, not only from a theoretical but also from a practical point of view. Although it is generally admitted that a sound knowledge of the technology of the dyes, mordants, &c., renders a vast assistance to the dyer, this must be increased two or threefold when it is combined with a thorough knowledge of the technology of the textile fibres, or at least with as complete a knowledge as our present scientific status will allow of, and the student will, therefore, see the necessity of devoting his close attention to this subject.

The textile fibres are usually divided according to their origin, and the great differences in their chemical and physical properties, into two great classes,* viz., *the vegetable fibres* and *the animal fibres*, which may

* In some works the *mineral fibres* form a third class. These comprise asbestos, glass wool, slag wool, &c., but as these fibres are of very minor importance in the textile industries (except as packing for steam joints, and for covering boilers and steam pipes), and are never submitted to any processes of dyeing or bleaching, they will not be considered in this work.

again be subdivided into several divisions, of which the most important member is usually taken as the typical representative.

Of the vegetable fibres cotton is the most important, and the fibre on which we possess the most detailed information. Then follow linen, hemp, jute, Chinagrass, and a host of other vegetable textile fibres, some of which have indeed met with a small demand in the market; while by far the greater number are merely museum specimens, and are likely to remain such. Although one sometimes comes across one of these fibres which, from the results of practical tests and experiments carried out on the small scale, promises good results as a textile fibre, the hold which cotton and linen have on the market almost invariably renders competition a practical impossibility. Of other vegetable substances which the dyer frequently has to deal with may be briefly mentioned: straw (for hats), vegetable ivory (for buttons), and wood. Paper, for the manufacture of which various vegetable substances are used, may vary considerably in its chemical properties according to the material from which it has been made.

The animal textile fibres include wool, hair, and the different kinds of silk. To the same class belong such substances as feathers, horn, bone, ivory, and leather. These substances are nitrogenous, and differ entirely from those of vegetable origin, not only in their chemical, but also in their physical properties; and, consequently, require a different treatment in bleaching, dyeing, and finishing. They will not withstand such high temperatures as those of vegetable origin; while at the same time they are more capable of resisting the action of mineral acids, but are much less stable towards alkalies than the latter. In addition to these properties, they have the power of combining directly with a much larger number of colouring matters, and possess the property of assimilating directly metallic bases from certain salt solutions.

THE VEGETABLE FIBRES.

COTTON (GERM., *Baumwolle*; FR., *Coton*.)

The working of cotton into fabrics originated, so far as we know, in India, the first allusions to cotton clothing extant being in Herodotus (B.C. 445). Some hundred years later we are told that the Hindoos wore "a sort of linen made from a stuff which grew upon trees." Pliny speaks of the Egyptians wearing cottons. The Chinese also used them. Spain was the first European country to manufacture cotton, and in the thirteenth century her products reached a high degree of excellence. The Dutch afterwards became very famous in the handicraft, and it is undoubtedly to the latter nation that we owe the success of the early manufacture of cotton in Great Britain. Probably the first mention of the trade in Lancashire and district is

contained in Lewis Roberts' *Treasury of Traffic*, published in 1641, in which, speaking of Manchester, the author says:—"Neither doth their industry rest here, for they buy cotton wool in London that comes first from Cyprus and Smyrna, and at home worke the same and perfect it into fustians, velveteens, dimities, and other such stuffes, and then returne it to London where the same is vended and sold, and not seldom sent into forrain parts, who have means at far easier terms to provide themselves of the said first materials."

Raw cotton, as it comes into the market, consists of the hairy material which covers the seeds of various species of the cotton plant (*Gossypium*), which belongs to the natural order of the Malvaceæ or mallow-worts. The fibres are attached to the seeds, which latter are enclosed in a 3 to 5 valved capsule. When ripe, this bursts and exhibits a ball of snowy white, or slightly yellowish fibre. The cotton is picked as soon as possible after ripening, and comes into the market after having been separated from the seeds by an operation termed "ginning." The seeds, which were formerly not considered of any value, are now used in the manufacture of cotton-seed oil, large quantities of which are at present used for soap making and other purposes. The complete separation of seed particles is not always possible, and they are frequently visible in grey calico in the form of black specks or "motes." These may, under certain conditions, give up part of the oil or tannin which they contain to those portions of the cloth which are in the immediate vicinity, and thus give rise to unevenness in dyeing.

There are four primary species of the cotton plant, which appear to include all those which are usually cultivated for commercial purposes. These are:—

(1.) *Gossypium Barbadosense*.—This is the most valuable, being the one which produces the long silky-haired Sea Island cotton. The *Gossypium hirsutum*, which is supposed to be a variety of this species, is the one from which the greater portion of the United States crop is raised. The former bears a yellow, the latter a white or faintly primrose flower.

(2.) *Gossypium Peruvianum* is indigenous to South America, and flourishes in Peru, Brazil, and the neighbouring countries. The flowers are yellow.

(3.) *Gossypium herbaceum* is a native of Asia, and is a small shrubby plant bearing a yellow flower. It produces the Madras, Surat, short-stapled Egyptian, and some qualities of American cotton.

(4.) *Gossypium arboreum* is also found in India and China, and is a fine tree-like plant, bearing a reddish flower, and yielding, under suitable conditions, a long silky cotton.

Practically considered, the best division is (according to Bowman) that of herbaceous, shrub and tree cotton. In one or other of these forms the plant is indigenous to the warm climates, but especially

to India, Egypt, and America. The herbaceous cotton is the most valuable, and is that from which the large American crop is obtained. The shrub is about the size of an ordinary curra. bush, and in the hottest climates becomes perennial.

Bowman defines the typical cotton fibre as a long tubular compound vegetable cell, from 1,200 to 1,500 times as long as it is broad. The

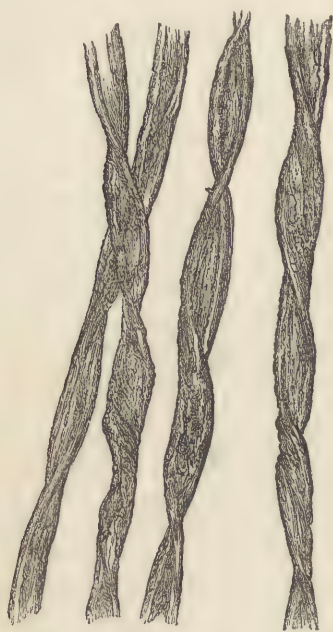


Fig. 1.—Typical cotton fibres.



Fig. 2.—Transverse sections of cotton fibre.

the fibres are indeed much longer, but stiff and straight.

In the perfectly ripe cotton, the tubular form is distinctly seen in section, but the young unripe fibres show no indications of a tubular



Fig. 3.—Transverse sections of unripe cotton.

structure. Under the microscope they present the appearance of broad ribbon-like fibres, which are almost transparent and show irregular folds. Such fibres, which are technically known as *dead cotton*, are difficult to dye, and may some times be met with in indigo or alizarin dyed calico in the form of white specks.

outer sheath appears to be a continuous liber cell of pure cellulose; and the inner or thickening layers of the tube consist of secondary cellular deposits upon this epidermic layer, or are formed by a gradual thickening of that layer itself. The thin end of the fibre is closed; while the other—viz., that by which it was attached to the seeds, is irregularly torn. When viewed under the microscope, the cotton fibres present the appearance of twisted ribbons, thicker as a rule at the edges than in the middle. This spiral shape of the fibre is due to the drying up of the sap originally contained in the ripe fibre. In transverse section, the normal cotton fibres present a great variety of shapes, but they are all more or less flattened, and in each is visible the small opening which runs from the base almost to the extreme end of the fibre. The special character of the fibre renders it suitable for the manufacture of very fine yarns;

and also accounts for the elastic character of fabrics made from cotton, as compared with linen fabrics, of which latter

fibres, which are almost transparent and show irregular

The length and diameter of the cotton fibres vary considerably according to their origin, as will be seen from the following figures quoted by Evan Leigh:—

Description of Cotton.	Length of Staple in Inches.		Diameter of Fibre in Inches.	
	Min.	Max.	Min.	Max.
New Orleans,	0·88	1·16	0·000580	0·000970
Long Stapled (Sea Island), .	1·41	1·80	0·000460	0·000820
Brazilian,	1·03	1·31	0·000620	0·000960
Egyptian,	1·30	1·52	0·000590	0·000720
Native Indian,	0·77	1·02	0·000649	0·001040

Expressed in millimetres, the mean length of the cotton fibre varies between 15 and 60 and the diameter from 0·010 to 0·040.

As a rule the longest fibres have the smallest diameter, and are finer and silkier in the staple; they can be spun to the finest counts, and command the highest price in the market. We obtain an idea of the minuteness of an individual cotton fibre when we remember that if all the fibres contained in a single pound of American cotton were placed end to end in a straight line they would reach 2,200 miles. The strength of the individual cotton fibres is also subject to considerable variations, as will be seen from the following figures, which represent the results of experiments carried out by Chas. O'Neill. He arranges them as follows:—

	Mean Breaking Strain in Grains.
Sea Island (Edisto),	83·9
Queensland,	147·6
Egyptian,	127·6
Maranham,	107·1
Bangueld,	100·6
Pernambuco,	140·2
New Orleans,	147·7
Upland,	104·5
Surat (Dhollerah)	141·9
„ (Comptah),	163·7

Speaking roughly, the fibre which carries the highest strain has the largest diameter, and, therefore, the largest sectional area to resist the breaking. The ripe fibres—that is, those in which the sectional area is greatest, are consequently able to resist a greater strain than the unripe fibres of one and the same quality. When subjected to tension, the walls have a tendency to collapse; and, when the flattening process has gone so far as to obliterate the whole of the central

opening, the extreme outer structureless pellicle seems to suffer rupture first, while the inner parts of the tube-walls seem to extend slightly, and then the whole completely severs. This severing is usually accompanied by a drawing-out of portions of the secondary deposits which remain, after the rupture is complete, in the form of fibrous masses, giving a very ragged edge to the fractured tube. In dyed yarns, which have the cellular spaces filled with microscopic crystals, the tendency to rupture seems (according to Bowman) to be increased by the sharp edges of the crystals penetrating the cell-walls when they are closed in upon the crystals by the extension of the fibre under the strain. A similar weakening effect is produced when cotton goods, after treatment with soda, are allowed to dry before the soda has been sufficiently removed by washing. The formation of soda crystals in the interior of the tubes appears to have a sufficient molecular force to burst the fibre. This bursting of the fibre is more marked in the formation of ice within the cell-walls. The water, which is sucked into the fibres by capillary attraction, expands considerably and, with an almost irresistible force when it changes into ice and thus bursts the fibres asunder. Advantage is taken of this phenomenon in the manufacture of filter-paper, in order to increase as far as possible the total surface of fibre, and make it retain finely-divided precipitates.

Up to a certain degree, the action of heat is such as to influence only the physical properties of the cotton fibre. Heated to 100° , the fibre loses its natural hygroscopic moisture, or (as Bowman terms it) its water of hydration, which amounts under ordinary circumstances to from 5 to 7 per cent. When exposed to the air again at the ordinary temperature the fibre rapidly regains weight until it has absorbed just as much moisture as it gave off. The rate of absorption varies, however (as might be expected), with the hygrometric condition of the air, being much slower in fine, dry weather than in foggy or wet weather. The maximum amount of hygroscopic moisture which the cotton fibre is capable of absorbing is, according to Wiesner, just under 30 per cent. At 100°C . the cotton fibre becomes plastic, although not to the same extent as is the case with wool and silk. The fibres may be made (under the influence of pressure) to assume at this temperature certain shapes, or may be made to lie in certain directions, retaining their position after cooling. On this property are based the various processes of hot-finishing (calendering, &c.)

Counts of Cotton Yarn.—The fineness of cotton yarn is expressed by so-called "counts," or numbers which indicate how many hanks of 840 yards each go to a pound. Thus by 60's cotton is meant a yarn, of which 60 hanks of 840 yards each would be required to make a pound.

Chemical Composition and Properties.—Cotton, freed from the natural impurities, which it invariably contains in greater or smaller quantities, consists of almost pure cellulose, a substance which is

universally distributed throughout the vegetable kingdom, and which forms (either as such or in some modified form) the so-called ligneous or woody fibres of plants. But whereas in the cotton fibre cellulose exists in an almost pure condition, it is otherwise generally accompanied by a greater or less amount of incrustaceous matter which is usually difficult to remove. The impurities contained in raw cotton amount to about 5 per cent. by weight; and consist, essentially, of pectic acid, colouring matter, cotton wax, cotton oil, and albuminous matter. The process of *bleaching* has for its object the removal of these substances, which will, therefore, be referred to again under that heading. Our first object is to study the chemical composition and properties of cellulose; and the action on it of the various chemical agents which it may come in contact with in the various processes of bleaching, dyeing, &c.

The chemical analysis of cellulose shows that it consists of carbon, hydrogen, and oxygen, and that the simplest formula representing its composition is $C_6H_{10}O_5$. It belongs to a naturally occurring important class of substances, which are chemically known as carbohydrates, of which starch, dextrin, and the sugars may serve as familiar examples. These bodies may be looked upon as polyatomic alcohols, containing at the same time aldehyde or ketone groups. According to recent investigations of Cross and Bevan, cellulose forms a penta-acetyl derivative and must consequently be regarded as a pentatomic alcohol, $C_6H_5(OH)_5$.

Pure cellulose is a somewhat inert substance; it is colourless, possesses neither taste nor smell, and is absolutely insoluble in water, alcohol, ether, and other ordinary solvents. Its specific gravity is about 1.5. When heated, it first parts with its water of hydration; and, if heated still further, it begins to turn brown at about $230^\circ C$.; but if strongly heated in closed vessels it is ultimately completely decomposed, yielding water, acetic acid, methyl alcohol, acetone, and other products similar to those obtained in the dry distillation of wood, and leaving behind a residue of charcoal. In the open air it burns freely without emitting any very strong smell, but smouldering cotton gives off the characteristic penetrating smell of acrolein.

Under ordinary conditions water has no action on the cotton fibre, but when heated under pressure to 150° with water, A. Scheurer finds that the fibre is sensibly attacked. Raw cotton subjected to this treatment for eight hours had decreased in strength from 18 to 17, bleached cotton from 27 to 20.

When treated with an ammoniacal solution of copper hydrate, the cotton fibre swells up considerably and slowly dissolves, forming a thick slimy solution, from which acids throw down a gelatinous precipitate. This, when washed and dried, forms an amorphous white powder possessing the same chemical composition and properties as the original purified fibre. It is, therefore, regarded as unchanged

cellulose. Recent researches by Prudhomme,* however, have shown that oxycellulose is formed by the action of ammoniacal copper solution on cellulose.

Behaviour towards Acids.—Concentrated mineral acids usually exercise a very powerful and rapid action on the cotton fibre, but this may vary considerably according to the kind of acid, temperature, and duration of contact.

Concentrated sulphuric acid first causes the cotton fibre to swell up, forming a gelatinous mass; and, if this is rapidly diluted with water, a precipitate is obtained of a substance termed *amyloid* which is coloured blue by iodine solution. The formation of vegetable parchment is supposed to be due to the partial transformation of the vegetable fibres into this substance. Vegetable parchment is prepared by passing unsized paper into cold sulphuric acid at 140° Tw., allowing it to remain in the liquid for not less than five, and not more than twenty seconds, and then thoroughly washing out the acid in plenty of water. Paper treated in this manner is found to have decreased in volume, but to have increased in density, while, at the same time, its strength has increased three to four fold. The same treatment is said to impart to the cotton fibre an increased affinity for the basic coal-tar colours.

By the continued action of strong sulphuric acid cotton is completely dissolved and is converted into a gum-like substance, chemically known as dextrin, which possesses the same composition—viz., $C_6H_{10}O_5$. If the solution is now diluted and boiled for some time, the dextrin undergoes a further chemical change and is converted into glucose or grape-sugar, $C_6H_{12}O_6$. The close relationship which exists between these three carbohydrates is thus shown in a striking manner.

By strong hot nitric acid, cotton is entirely decomposed, a number of products being formed, including oxalic acid and an oxidised cellulose soluble in alkalies. Towards a mixture of strong nitric and sulphuric acids, or towards cold nitric acid, the cotton fibre behaves in a different and somewhat peculiar manner. Its external appearance is not changed, but the cellulose becomes converted into a series of compounds, which are known as nitro-celluloses, and which contain more or less nitrogen, according to the strength of the original mixture of acids and the duration of the immersion. If cotton is passed through cold strong nitric acid it is converted into dinitro-cellulose, the fabric neither being rendered inflammable nor tender. Cotton treated in this manner shows a direct affinity for the basic colouring matters (H. Koechlin). These bodies were first discovered in 1846 by Schönbein. The most highly nitrated product hitherto described has the composition $C_{12}H_{14}(NO_2)_6O_{10}$, and is known as *pyroxylin* or *gun-cotton*. A less nitrated product (trinitro-cellulose), produced by the action of less concentrated acids on cellulose, is known as *soluble*

* *Journ. Soc. Dyers and Col.*, 1891, p. 148.

pyroxylin. It is soluble in a mixture of ether and alcohol; the thick solution thus obtained constitutes the so-called *collodion*. When allowed to evaporate, collodion leaves behind a thin horny layer which is transparent and insoluble in water; it has been used extensively on this account in photography, and to some extent for surgical and other purposes.

If a solution of tetra-nitrated cellulose in a mixture of alcohol and ether be forced through a very small orifice into water, it instantly solidifies, and a continuous fibre can be drawn from the orifice which in its external appearance resembles silk. M. de Chardonnet, who was the first to notice this interesting fact, has turned it to practical account for the manufacture of so-called *Artificial Silk*, which was practically demonstrated on the small scale at the Paris Exhibition of 1889. The pyroxylin employed is a tetranitro-cellulose, which is first dissolved in a mixture of 38 parts ether and 42 parts alcohol so as to form a 6.5 per cent. solution. This latter is introduced into a small tinned copper vessel, from which it is forced by means of a continuous air pressure through a vertical glass tube (C), (Fig. 4), ending in a fine capillary orifice (A), and surrounded by another glass tube (B), through which there is a continuous flow of fresh water. As soon as the pyroxylin solution comes in contact with the water it solidifies, and may be reeled off in the form of a continuous fibre. Instead of one, two or more glass orifices may be fed from the same copper vessel; and the threads may either be reeled separately, or may be combined and reeled together. By the addition of certain colouring matters (*e.g.*, safranine) to the collodion solution, uniformly coloured threads can be obtained. In consequence of the highly inflammable nature of pyroxylin, it is necessary to denitrify the product. This is effected (although not completely) by a treatment with dilute nitric acid; but, by a further treatment, with phosphate of ammonia, the fibre is said to be rendered sufficiently unflammable for all ordinary purposes. Artificial silk has, according to M. de Chardonnet,* a specific gravity of about 1.49, and will bear a tensile strain of 25 to 35 kilos per square millimetre of sectional area. The diameter may vary from 0.001 to 0.040 mm. The brilliancy or gloss of the fibre surpasses that of ordinary boiled-off silk. Artificial silk may be dyed like ordinary silk, but care must be taken not to have too high a temperature in the dye-bath.

By strong hydrochloric acid cotton is disintegrated, especially when the material is dried with the acid in. It is thus reduced to a white powder.

Dilute mineral acids have little or no action on cotton when cold.

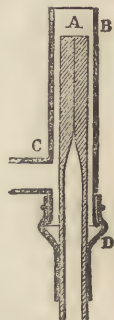


Fig. 4.
Artificial
silk spin-
neret.

* *Comptes rendus*, cvii., p. 562.

If cotton is exposed at the ordinary temperature for a few minutes to the action of sulphuric acid of from 104° to 125° Tw., and is then thoroughly washed, the strength of the fibre is (according to Mercer) not impaired; but it acquires an increased affinity for colouring matters. In the cold, sulphuric acid only changes the fibre when it is sufficiently concentrated to absorb more water with evolution of heat. According to C. Koechlin,* one may steep cotton in acid at 32° to 52° Tw., at 15° C., and it will only be at 69° Tw. (3 parts acid to 8 parts water by volume), that the change is noticeable after the third hour. Cotton can withstand the action of sulphuric acid at 93° Tw., diluted by its own volume of water for one hour. In six hours the fibre is tendered and begins to absorb colour from a solution of methylene blue; in forty-eight hours, the change and property of absorbing colour are complete.

With sulphuric acid, containing 100 grms. per litre and heated to 80° C., no immediate change is effected; it takes five minutes for the change to begin, thirty minutes before it has made progress, and an hour for completion.

If cotton, saturated with dilute mineral acid be allowed to dry, the acid gradually becomes more and more concentrated on the fibre, and the latter is "tendered." The degree to which the tendering takes place will depend to a great extent on the temperature at which the drying is effected. Sharp drying at a high temperature has a much more destructive influence than slow drying. The same takes place when cotton impregnated with certain salts, such as the chlorides or nitrates of aluminium, iron, or chromium is dried. A more or less complete dissociation of the salt takes place and the acid which is liberated tenders the cotton. Hence, it is obvious that all cotton goods or goods containing cotton should be well washed after being in contact with mineral acids, however dilute, or with salts, which are liable to undergo dissociation, in order to avoid tendering in the drying operation. When viewed under the microscope the tendered fibres do not appear to have undergone any physical change, but analysis shows that a chemical change has taken place, which consists of a slight increase in the percentage of hydrogen and oxygen. If the acid is taken strong enough the cotton is completely disintegrated on drying, and falls to a white powder which contains half a molecule of water more than ordinary cellulose, and is known as *hydrocellulose*.

Advantage is taken of this property in the process of *carbonising* or *extracting*, the object of which is to remove the cotton and linen from woollen rags in the manufacture of shoddy and mungo or for getting rid of "burrs" in loose wool as well as flannel and other all-wool piece-goods.

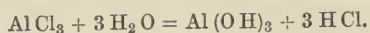
Carbonising.—Woollen rags or loose wool are immersed for 2 to 12 hours in dilute sulphuric acid at from 2 to 8° Tw., the duration of

* *Journ. Soc. Dyers and Col.*, p. 103, 1888.

the immersion depending upon the strength of the acid. After the excess of acid has been removed in hydro-extractors, the rags are carefully dried, first at a temperature of 30° to 45°, which is raised after 2 to 3 hours to 70° to 80°, at which temperature the vegetable fibre is carbonised. The material is now taken out, and the vegetable fibre, which crumbles to dust by friction, is mechanically removed.

According to another method, which is sometimes employed for rags in the production of shoddy or mungo, the material is exposed to the action of dry hydrochloric acid gas in a revolving cylindrical cage which is contained in a cylindrical cased iron vessel heated by steam to about 100°.

Aluminium chloride is also used for carbonising. The action depends upon the fact that when an aqueous solution of aluminium chloride is evaporated to dryness, it is decomposed with the formation of alumina and free hydrochloric acid according to the equation:—



The liberated hydrochloric acid acts powerfully on the vegetable fibre, which is destroyed, as in carbonising with sulphuric acid. The carbonising temperature for aluminium chloride is higher than for sulphuric acid.

Piece goods are carbonised either by means of sulphuric acid or aluminium chloride. The following is an interesting application of the process of carbonising with aluminium chloride. Goods manufactured from mixed yarns of cotton and wool are printed in patterns with thickened aluminium chloride, and dried in the carbonising stove. The effect of this is that the cotton is destroyed in those portions of the fabric which were in contact with the aluminium chloride, and there the fabric becomes so impoverished as to produce a gauze pattern. By subsequently dyeing the cotton, or the wool, or both, in various colours, beautiful effects can thus be obtained.

Organic acids have under ordinary circumstances no injurious effect on the cotton fibre, but when steamed under pressure with oxalic, tartaric, or citric acids, the fibre is liable to become tendered. Acetic acid has no injurious action whatever.

Behaviour towards Alkalies.—The action of alkalies on cellulose is very different to that of acids. Alkaline carbonates, and the milder alkalies, such as soap, borax, phosphate of soda, &c., have no action. Nor has ammonia under ordinary circumstances any effect on the cotton fibre. But if (according to L. Vignon) cotton is heated under pressure with strong aqueous ammonia, or the compound of ammonia and calcium chloride, to 200°, a nitrogenous product is obtained which, although not differing from the original in external appearance, behaves towards the acid dyes like an animal fibre.

Dilute caustic alkalies or lime do not affect the fibre if, during the operation, air be excluded; but in presence of air and at high

temperatures the fibre is converted partially or wholly into *oxy-cellulose*, and its tenacity is thus impaired. This circumstance is liable to give rise to faults in bleaching, and care must, therefore, be taken when boiling the cotton goods with lime or alkali to exclude the air or to deprive it of its oxygen by means of some reducing agent.

Under the influence of concentrated caustic alkalies, cotton is changed both physically and chemically. John Mercer, a Lancashire calico printer, first studied, as long ago as 1844, the action of these reagents on the cotton fibre, and to him we are chiefly indebted for our knowledge of the subject. He first noticed the change in endeavouring to filter strong caustic soda solution through cotton cambric. The solution passed through very slowly, and the density of the filtered liquid was only 53° Tw., whereas that of the original solution was 60° Tw. At the same time the cloth had become semi-transparent, contracted both in length and breadth, and thickened. Cotton thus treated was found, after the alkali had been removed by washing, to have gained in weight and in strength; and, further, it possessed an increased affinity for colouring matters. Sulphuric acid and chloride of zinc have, under certain conditions, a similar action on cotton. Their use is included in Mercer's Patent Specification, granted in 1850 for "improvements in preparation of cotton and other fabrics and fibrous materials." The process is now generally known as the mercerising process. Mercer obtained the best results by immersing the cotton cloth (which had been previously bleached, without being boiled, in weak alkaline liquors) in caustic soda at 45° to 50° Tw.; but the change is sufficiently marked with ordinary bleached calico. The linear contraction is found to be from one-fifth to one-fourth, and it was possible thus to contract fine cotton cloth containing 200 picks to the inch to reach within 270 picks to the inch. Experiments made with regard to the increase in strength showed that a strip of calico which required before treatment a weight of 13 lbs. to break, required after treatment no less than 22 lbs. A bundle of threads which showed a breaking strain equal to 13 oz. before treatment, required, after treatment, 19 oz. to rupture them.

The increase in weight amounted from 4·5 to 5·5 per cent. of the weight of the original cloth. The increase is due to the presence of water in excess of the ordinary hygroscopic moisture contained in the original fabric. At 100° this water is driven off along with the hygroscopic moisture, but is taken up again when the fabric is exposed to the air. Mercer's explanation of this chemical change is that the cellulose forms, while in contact with the caustic alkali, a compound, $C_{12}H_{20}O_{10} \cdot Na_2O$, which is decomposed by water into a hydrated cellulose, $C_{12}H_{20}O_{10} \cdot H_2O$.

The increased affinity of mercerised cotton for the colouring matters

is another interesting feature in the process. It is especially striking in the case of the direct cotton colours; and can be readily observed by dyeing together two materials of bleached calico (one mercerised, the other not) in benzopurpurin for example. The colour produced on the mercerised pattern will be much fuller and deeper than on the ordinary calico. Mercerised cotton also has an increased affinity for tannin substances.

The microscopical appearance of the cotton fibre before and after mercerising was studied by Walter Crum. By examining cross-sections of these fibres, he found that the action of the process was to cause the flattened fibre to assume the round solid form of ripe cotton, while at the same time the central opening



Fig. 5.—Cross-section of mercerised cotton fibres.

is decreased in size. The contraction of the mercerised fabric is due to the twisting of the fibre under the influence of the alkali.

The fact that a French company offered Mercer the sum of forty thousand pounds for the purchase of his patent rights, is sufficiently indicative of the importance which was at the time attached to his discovery. But, in spite of its advantages, the process has never been extensively used on the large scale. This appears to be principally due to the surface contraction, which was inevitable; and which not only increased the price of the material, but did not suit the merchants and manufacturers. Mercerised cotton blankets are largely used in calico-printing on account of their superiority in point of cheapness and durability over those made from wool.

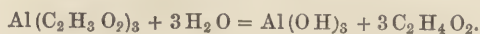
Behaviour towards Reducing and Oxidising Agents.—

Reducing agents appear to have little or no action on cellulose, but energetic *oxidising agents* (like chromic acid, permanganate of potash, chlorine, chloride of lime, air in presence of alkalis, &c.) readily convert it into *oxycellulose*, a product first described by Witz and subsequently studied by Cross and Bevan. The most striking property of oxycellulose is its affinity for the basic colouring matters, with which it can be dyed without the intervention of a mordant. Practically, the formation of this interesting product can be readily demonstrated by printing calico with a moderately concentrated thickened solution of chloride of lime, washing the material well after some time, and then dyeing in a solution of methylene blue. The printed portions will be more or less of a dark blue, according to the duration of the action, while the untouched parts will only be tinted. By boiling cotton for a short time in a dilute alkaline solution of permanganate of potash and subsequently decolourising it in a solution of bisulphite of soda, a similar change can be effected. The formation of oxycellulose has little practical importance, owing to the fact that the fibre is thereby considerably tendered. The

tendering is especially noticeable after treatment in hot alkaline (soap, &c.) solutions. This difficulty is frequently met with in the production of white or coloured discharges on indigo-dyed calico in printing. For producing a white design, for instance, thickened chromate or bichromate of potash is printed on the fabric which, after drying, is passed through a solution of sulphuric and oxalic acids. The chromic acid thus liberated destroys the indigo, producing a white design; but, at the same time, the fabric becomes so altered in the discharged places, that a subsequent treatment in boiling soap solution tenders it.

By prolonged action, or where present in great excess, these oxidising agents may completely rot the fibre. Such is the case when, in bleaching, small particles of undissolved chloride of lime get into the material; wherever a particle has embedded itself in the material, a hole is likely to be burnt through. The dyer or bleacher has, therefore, to use due discretion in treating cotton with these chemical agents.

Behaviour towards Mordants and Colouring Matters.—The cotton fibre has little or no affinity for ordinary metallic salts like alum, copperas, copper sulphate, &c.; but, when they are present in solution in a very basic condition, it is capable of decomposing them and loosely fixing the metallic hydroxides. Advantage is seldom taken of this method of mordanting, except in printing, where the material is not unfrequently first padded with a solution of some decomposable salts, like the acetates, and then steamed. Thus if calico is padded in a solution of aluminium acetate, the alumina would be precipitated on the fibre in steaming, according to the equation:



The only mordants which appear to have a direct affinity for the cotton fibre are the tannins (*q.v.*); and these are used in immense quantities in cotton dyeing.

Until within the last few years, the only dyes for which cotton showed a direct affinity were—indigo, turmeric, safflower, and annatto. Some of the basic dyes, such as safranine and methyl violet, have, indeed, a slight affinity for cotton, and are used (when fastness is not a desideratum) for the production of light shades without the intervention of a mordant. But with the discovery of Congo red by Böttiger in 1884, the practice of cotton dyeing may be said to have entered upon a new era. The discovery of this new product was rapidly followed by numbers of others, commercially known as “benzidine dyes” or “direct cotton dyes,” with which we are at the present time able to produce any shade, except bright blues and bright greens. The majority of the direct cotton dyes are applied in an alkaline bath.

FLAX, LINEN (GER., *Flachs*, *Leinen*; FR., *Lin*).

Linen, which is the product of the flax plant, ranks next to cotton in importance among the vegetable fibres. The flax plant most generally cultivated is the *Linum usitatissimum*. Flax thrives best in a temperate climate. The seeds are sown either in spring or in summer, the former yielding the finer quality.

The first operation which the flax undergoes, after having been pulled from the ground, is that of *rippling*, which has for its object the removal of the seeds by drawing the plant through coarse iron combs. The seeds are used for the preparation of linseed oil. At this stage the air-dried product contains 73 to 80 per cent. by weight of wood, pith, and rind, and only from 20 to 27 per cent. of fibre. In consequence of the tenacity with which the bast fibres of flax adhere to the woody portion of the stem, its separation is tedious and involves several operations. The first of these is the *retting*, the action of which depends upon a species of fermentation. It may be carried out in various ways, viz. :—

- (1) By steeping in stagnant water ;
- (2) By steeping in running water ;
- (3) By dew retting ;
- (4) By artificial retting.

1. *Retting in stagnant water* is carried out chiefly in Russia and Ireland. It consists in steeping the flax in ponds or pits, from which the water can be let off when desired. The fermentation which takes place is accompanied by the formation of much soluble organic matter, and also by an intensely disagreeable smell. If care is not taken the fermentation is liable to become excessive and the fibre is weakened by overretting. The water used for this kind of retting should be soft, hard water being unsuitable. The retting is completed by exposing the flax in fields to atmospheric action for a week or so, a process which is known as *grassing*. Flax retted in this manner is of a dark colour.

2. The process of *retting by steeping in running water* is carried out principally in France, Belgium, and Holland. The flax is packed in large wooden crates and immersed in the running water. The fermentation sets in after a few days, when the flax is taken out, allowed to dry, and returned to the crates. The duration of the process may last from ten to twenty days. Flax retted in running water is of a much lighter colour than that retted in stagnant water.

3. *Dew retting* consists in exposing the flax in a moist state in fields for periods extending to ten weeks. The same kind of fermentation ensues as in the preceding process. Dew retting is used largely in Russia and Germany.

4. The artificial processes of retting may be sub-divided into—

- (1) Retting in tepid water ;
- (2) Retting with steam or hot water ;
- (3) Retting with mineral acids.

Retting in Tepid or Warm Water has for its object the acceleration of the process of fermentation. The flax, tightly bound up in bundles, is immersed in water having a temperature of 25° to 35°. The process lasts only two or three days. By passing the stalks, after the operation, through squeezing rollers, the greater part of the slimy matter adhering to them is removed, and the separation of the fibre from the woody portions is thus considerably facilitated.

Retting with Steam or Hot Water.—According to the process of W. Dogny,* the flax is first treated with water in iron cylinders at a temperature of 150°C. for twenty to forty minutes, and is then exposed for some thirty minutes longer to the action of dry high-pressure steam at the same temperature. This process, when the temperature and duration of the action are kept right, is said to give a complete retting by converting the pectose into pectic acid, leaving the flax firm, and giving it a silk-like lustre. The whole process, including drying, takes only a few hours.

Retting with Mineral Acids.—The addition of sulphuric acid in retting in stagnant water is said to obviate the disagreeable smell which is produced during the second part of the retting process.

According to another method, proposed by R. Baur, the crushed flax is steeped in water until it no longer yields to the latter any yellow colour. It is then drained and steeped for two to three days in water containing 3 per cent. of its weight of crude hydrochloric acid. The process is now practically over, and it only remains to neutralise the acid by passing the material through a weak alkaline bath.

After retting by any of the above processes, the flax is washed in water, and dried either in the air or by artificial means.

The quality and the chemical composition of the flax vary considerably, according to the process used in retting. Thus a flax retted by the Belgian process contained 82·5 per cent. of cellulose, and 7·6 of sugar ; while one obtained by retting in warm water was found to contain 88 to 89 per cent. of cellulose, and only 1 to 2 per cent. of sugar.

After retting, the flax is subjected to several mechanical operations, the object of which is to remove the woody portions of the stem as completely as possible.

The first of these operations is the *breaking*, by which the woody portion of the stem is broken up so as to facilitate its removal in the next operation. Breaking may either be done by hand, with the help

* *Journal Soc. Dyers and Col.*, 1888, p. 131.

of a simple contrivance, or by passing the stalks through a pair of fluted rollers.

In the next operation, that of *scutching*, the particles of wood are beaten out either by hand or machinery.

Next comes the process of *heckling*, the object of which is to lay the fibres parallel. This is effected by drawing the flax in bundles, first through coarse combs, then through finer and finer combs, until it is in a suitable condition for being spun. The combed or heckled flax is technically known as *flax-line*.

Counts.—In linen yarn the counts indicate the number of *leas* to the pound. A lea consists of 300 yards.

Composition and Structure.—Although consisting, like cotton, essentially of cellulose, linen differs materially from the latter fibre in its physical properties. As they occur in the raw material, the individual or ultimate fibres are gummed tenaciously together, but by treatment with dilute chromic acid they can be separated. Under the microscope these individual fibres are seen in the form of long cylindrical vessels which terminate conically at each end. The cell-walls are very thick, and the lumen is so small as to be indicated only by a thin black line. The mean length of the ultimate flax fibre is 20 to 40 mm., the breadth ranging from 0.012 to 0.026 mm., but generally the latter remains within the limits of 0.015 to 0.017 mm. During the operation of breaking, many of the fibres are torn or broken, and are then seen under the microscope to have jagged ends, which were formerly supposed to be notches in the fibre.



Fig. 6. — Microscopic appearance of linen fibre.

Flax is a better conductor of heat than cotton, and this is the reason why linen articles are colder to the touch than cotton. Besides, linen is stronger and more durable than cotton, and possesses a peculiar lustre. Air-dried linen contains 6 to 8 per cent. of hygroscopic moisture.

Chemically, linen consists essentially of cellulose, but the amount of impurities contained in the raw flax is much greater than in raw cotton, varying from 15 to 30 per cent. by weight. In Schweitzer's reagent, linen dissolves readily. Sulphuric acid and iodine colour it blue; sulphate of aniline has no action.

Towards chemical reagents generally linen behaves like cotton. In bleaching it requires a longer and more complicated treatment, owing to the difficulty of removing the large amount of pectic substances which the raw fibre contains.

Towards the dyes and mordants, linen behaves like cotton; but it is more difficult to dye than the latter. This difference is possibly

due to the difference in the physical structure of the two fibres; according to another view it is due to the presence of pectic substances in the linen.

HEMP (GER., *Hanf*; FR., *Chenvre*).

This fibre is the bast of the hemp plant, *Cannabis sativa*, which is cultivated in most temperate climates. The treatment of the hemp stalks is quite similar to that of flax, and includes rippling, retting, breaking, scutching, and heckling. Hemp is used principally for the manufacture of ropes, canvas, and sacking; for which purposes the fibre is eminently suited on account of its tenacity and the fact that it does not easily rot under water. It is seldom bleached or dyed; for, although this is possible, the fibre is too coarse to compare favourably with linen.

The ultimate fibres of hemp resemble those of linen in their appearance under the microscope, and have a diameter of 0.015 to 0.021 mm. The raw hemp fibre contains about 70 per cent. of pure fibre, the rest consisting of lignified or incrustaceous substances, wax, extractive matter, hygroscopic moisture, and ash.

JUTE.

After cotton, flax, and hemp, jute may be considered the most important vegetable fibre. It is the product of different species of *Corchorus*, plants indigenous to India. The most important species is the *Corchorus capsularis*, which is cultivated largely in most of the tropical climates of Asia.

When pulled the plants are stripped of their leaves, twigs, and fruit capsules, and are left lying for a few days in sluggish streams. This simple retting suffices to cause the bark to part from the stem, when it is stripped, rinsed in water, and dried in the air. The fibre thus obtained is very clean and comparatively pure. It comes into this country in the form of bundles. The length of the raw fibre is from $1\frac{1}{2}$ to $2\frac{1}{2}$ yards. About a foot of the bottom ends is cut off, and forms, as jute butts or jute cuttings, a valuable material for paper-making. The rest, after having been softened with an emulsion of oil in soap, is heckled and spun.

The ultimate jute fibres, which can be readily isolated from each other by means of caustic potash or dilute chromic acid, consist of bast cells, which vary in length from 0.8 to 4.1 mm., and in diameter from 0.01 to 0.032 mm. The transverse section of these cells usually appears pentagonal or hexagonal, the lumen varying in size, from a large internal opening to a mere speck.

Jute differs considerably from the vegetable fibres hitherto considered in its chemical composition and properties. It contains no

free cellulose, but consists, according to Cross and Bevan, of a chemical combination of bastose and cellulose, to which these authors have given the name of *Corchorobastose*. This substance shows the reactions of lignified tissue; it is coloured an intense brown by sulphuric acid and iodine, and a dark golden yellow by sulphate of aniline. If treated with chlorine and then with sulphite of soda, the jute fibre is coloured a beautiful crimson; tanned cotton behaves in a similar manner. Jute absorbs chlorine and bromine with avidity, and becomes chemically changed; the ordinary process of bleaching with chloride of lime is, therefore, not applicable to this fibre. By heating with bisulphite of soda under pressure the tendency of the fibre to rot is considerably lessened, and it is also thus rendered less liable to become discoloured.

Action of Water.*—Six hanks of bleached and unbleached yarn were dried in a water oven until a constant weight was obtained and then treated in the following manner:—

No. 1	steeped	$\frac{1}{2}$	hour	in	cold	water.
" 2	"	1	"	"	"	"
" 3	"	2	"	"	"	"
" 4	"	$\frac{1}{2}$	"	"	boiling	water.
" 5	"	1	"	"	"	"
" 6	"	2	"	"	"	"

Each hank was then dried, weighed, and the strength tested. In the first three cases, the yarn lost about 2 per cent. (exclusive of hygroscopic moisture); whilst with the last three, each lost about 3.5 per cent., very little difference being obtained between Nos. 5 and 6. With the grey yarn the average loss was about 1 per cent. for Nos. 1, 2, and 3, and 1.7 per cent. for Nos. 4, 5, and 6; but, whereas with the bleached yarn considerable darkening had taken place, depending upon the time of treatment, this was not noticed with the unbleached yarn. On testing the strength, however, although each hank was found to be tendered, this was not so marked as anticipated, since No. 1 differed very little from Nos. 4, 5, and 6; but in the three latter cases each fibril was more matted together and the yarn had also shrunk in length considerably.

Action of Sulphuric Acid.—Similar hanks, as in the last experiment, were taken and—

No. 1	steeped	in	1	per	cent.	H_2SO_4	for	30	minutes,	at	100°	C.
" 2	"	"	3	"	"	"	"	"	"	"	"	"
" 3	"	"	6	"	"	"	"	"	"	"	"	"
" 4	"	"	1	"	"	"	"	for	60	minutes,	"	"
" 5	"	"	3	"	"	"	"	"	"	"	"	"
" 6	"	"	6	"	"	"	"	"	"	"	"	"

After treatment they were thoroughly washed and dried, Nos. 1 to 3 (unbleached yarn) lost about 2.8 per cent. in weight, and Nos. 4 to 6,

* We are indebted for this information to Mr. J. R. Appleyard, F.C.S., of University College, Dundee.

3·6 per cent.; but, as regards the strength, only Nos. 5 and 6 were found to be very much tendered, so that 3 per cent. sulphuric acid seems to have as much effect upon the yarn as 6 per cent.; this result is also substantiated on the large scale. But after jute has been treated with sulphuric acid, although the tendering produced, as shown by an ordinary testing machine, may appear very slight, still it is sufficient to cause serious effects during the spinning process, probably because each fibril, although itself very little tendered, is rendered more brittle, and thus by the constant working of the loom very soon breaks. After treatment with sulphuric acid the bleached yarn has a more glossy and silky appearance, whilst the unbleached yarn is turned more of a pink colour.

According to Cross and Bevan, when jute is treated with 5 per cent. sulphuric acid, at a temperature of 80° to 90° C., it is slowly acted upon with the production of a body, soluble in alcohol, which is also a carbohydrate; the remaining portion is altered in appearance and fracture takes place across the fibre.

Action of Alum.—In this experiment the yarn was steeped in the boiling solution of the alum, and, after treatment, was well washed and dried.

No. 1 steeped in 5 per cent. Alum for 30 minutes.

„ 2	„	10	„	„	„
„ 3	„	20	„	„	„
„ 4	„	5	„	„	60 minutes.
„ 5	„	10	„	„	„
„ 6	„	20	„	„	„

On testing the strength of each hank very little difference was noticed between Nos. 1, 2, 3, 4, 5, and 6, deducting of course the amount of tendering which the yarn would undergo if steeped in boiling water for the same length of time, so that it is advisable, whenever possible, to use alum in place of sulphuric acid in dyeing.

In dyeing, jute distinguishes itself by its natural affinity for the basic and some of the acid colouring matters. It is used largely in the manufacture of carpets, matting, sack-cloth, &c.

Counts.—For jute yarn, the counts are the same as for linen.

CHINAGRASS (GER., *Nessel*; FR., *Ramie*).

This fibre, also known under the name of Rhea or Ramie, is the bast fibre of a kind of nettle, botanically known as *Boehmeria nivea*, which is largely cultivated in China, India, and other countries. The annual exports of this fibre from China alone amount to almost 3,500 tons.

The great difficulty in the production of this fibre lies in the fact that no suitable method has hitherto been devised for separating the bast from the stem and bark. The process of retting as carried out

with flax, hemp, and jute is (according to O. N. Witt) not suitable, since, after a very short time, the bast is so completely separated into its ultimate fibres that the latter cannot be recovered coherently, but become so entangled with the other portions of the stem that their subsequent separation is practically impossible.

The usual process adopted is to separate the bast from the stems while the latter are still green. This can be readily effected by hand or by the machine constructed for this purpose by Messrs. Death & Ellwood of Leicester. In this the green stems are pushed against a revolving beater which breaks the woody part of the stem. The removal of the broken wood and the washing of the raw fibre are effected by means of a powerful jet of water.

After standing for some time the fibre becomes so firmly attached to the woody portion of the stem that it cannot be completely detached, and, as this is almost inevitable in hot climates, like India, various remedies have been recommended to counteract this evil. According to Favier the fibre may be readily separated from the dried stems by steaming them for 15 to 30 minutes in wooden boxes. Sansone recommends the treatment of the dried stems for 20 to 30 minutes in a boiling solution of carbonate of soda or of caustic soda, or the storing of the green stems in pits containing a solution of bisulphite of soda or sulphurous acid by which fermentation is prevented.

The individual fibres of the Chinagrass obtained from *Boehmeria nivea*, possess a maximum length of 22 centimetres and a diameter which varies from 0.04 to 0.08 millimetres. The raw fibre contains, according to Hugo Müller, 78 per cent. of cellulose and 6 per cent. of intracellular substances and pectic matter. In the purified state the Chinagrass fibre is characterised by its beautiful silk-like gloss, which is superior to that of linen. For the basic colouring matter it exhibits a slight affinity. Although easy to bleach, it is difficult to dye it in full bright shades without injuring the characteristic lustre of the fibre.

OTHER VEGETABLE FIBRES.

The most important vegetable fibres have already been mentioned; but a host of others are known, only a few of which are used in this country. The most important are:—Manilla hemp, Sunn hemp, Sida fibre, New Zealand flax, and the fibres obtained from the leaves of the aloe, the agave, the banana, the palm, and the fibrous material which surrounds the cocoa nut. As these fibres are seldom dyed and the exact information regarding them is somewhat scanty, they will not be further considered in this work.

THE ANIMAL FIBRES.

WOOL (GER., *Wolle*; FR., *Laine*).

Strictly speaking, wool is the hair of the sheep, but the hair of certain goats—*e.g.*, Cashmere, Mohair, and Alpaca—and of the camel are generally classed under the same category. Hair only differs from wool in its physical structure.

Some naturalists assume that there are only three original species of sheep, viz. :—

The *Ovis ammon* or argali, the wild sheep of Asia and America; the *Ovis musmon*, indigenous to the south of Europe and the northern parts of Africa; and the *Ovis aries*, or domestic sheep, which is the principal English variety.

From an industrial point of view, Archer distinguishes no less than 32 different varieties, of which 4 belong to Europe, 15 to Asia, 11 to Africa, and 2 to America. All these varieties give rise to different qualities of wool, which are distinguished from each other by the length, fineness, strength, elasticity, colour, curl, &c., of the fibres. The wool not only varies in quality with different animals, but also on one and the same individual. The best is that from the shoulders, the lower part of the neck, the back, and the upper part of the sides, while that which covers the head, tail, belly, and legs is of an inferior quality. The separation of the various qualities of wool from each fleece can only be done by hand, and the operation is known as *wool-sorting*.

It would be useless to detail here on the large number of different qualities of wool which come into the market. The diameter of the fibre is, as a rule, proportional to its length, *i.e.*, the shorter the staple, the finer the fibre and *vice versa*. The dyer usually distinguishes between the coarse and long-stapled *lustre wools*, most of which are produced in this country; and the finer qualities of *merino* or *cross-bred* wools, which are imported principally from Australia, and go under the general name of *Botany* wool. In addition to these, the following should be specially mentioned :—

The *Cashmere* wool of India, which is the produce of a goat which abounds in the mountains of Thibet. The hair of this animal sometimes reaches 18 inches in length.

Mohair, which is the wool of the Angora goat, is imported into this country chiefly from Turkey and the Cape. Mohair is characterised by its striking lustre.

Alpaca, the hair of a goat which belongs to a genus of which the Llama is the best known. Closely allied to this is the so-called *Vicuna* wool.

Camel's Hair.—The camels, which abound as domestic animals in many hot climates (especially in the northern parts of Africa), cast

their hair periodically; this is collected, and comes into the market as a textile material.

Fur consists principally of the hair of the hare and the rabbit, and is extensively employed in the manufacture of better class felt for hats.

The wool of diseased sheep, or of such as have died from disease, is of inferior quality to that taken from the living animal. It also behaves differently in dyeing. Bosc gives an interesting account of an experiment carried out by him with the wool of three Rambouillet sheep, all of the same age and race. The first was in robust health, the second diseased, while the third had died of disease. Each fleece was washed separately and spun into yarn. The yarn was made up into hanks and dyed at the Gobelins in three shades, viz., blue, red, and yellow. The colours of the hanks made from the wool of the healthy sheep were bright, of the diseased sheep of a lighter shade,



Fig. 7.—Appearance of worsted (a) and woollen (b) yarn under the microscope.

and those from the dead sheep dull. In dyeing each colour, all three samples were dyed in the same bath.

The wool from slaughtered sheep, if removed from the skin by cutting, is not inferior in quality to that shorn from the living animal. But the usual process for removing the wool from the skins is to steep the latter for a time in lime water or dilute solution of sodium sulphide. This causes the fibres to become so loosened at their roots that they can be readily removed. The wool obtained in this manner is generally known as “pulled wool,” and is inferior in quality to that obtained from the living animal.

Wool comes into the market in a large number of different qualities; some has been washed on the sheep's back before the clip, but the greater portion of what is offered for sale is “in the grease.”

According to its length of staple, wool generally is divided into long-stapled and short-stapled qualities. In the process of combing, to which most wools are subjected after being sorted and washed, before being spun, these fibres are separated. The long-stapled fibres (exceeding $1\frac{1}{2}$ inches in length) are usually made up into *tops*, and are afterwards spun on ring- or cap-spinning frames into *worsted yarn*; the shorter fibres, the so-called *noils*, are carded and spun on mule spinning frames into *woollen yarn*. Worsted yarn is used principally in the manufacture of coatings, worsted trousers, and ladies' dress goods, which require little or no milling. Woollen yarn, on the other hand, is used principally in the manufacture of goods which are subsequently milled for the purpose of producing to a greater or less degree a felting of the fibres. In worsted yarn, the fibres lie more or less parallel to each other, and the diameter of the yarn does not vary much, while in woollen yarn, the fibres lie pretty well in all directions, and the diameter of the yarn is very irregular (see Fig. 7).

Counts.—In worsted and Mohair yarns, the counts indicate the number of hanks of 560 yards each to the pound.

For woollen yarns they are different. In Yorkshire, the counts are generally the number of yards per dram, but in Dewsbury they indicate the number of yards per ounce. In the West of England the woollen counts indicate the number of hanks of 320 yards each to the pound.

Structure of the Wool Fibre.—When seen under the microscope, the cleansed and white wool fibre appears in the form of a

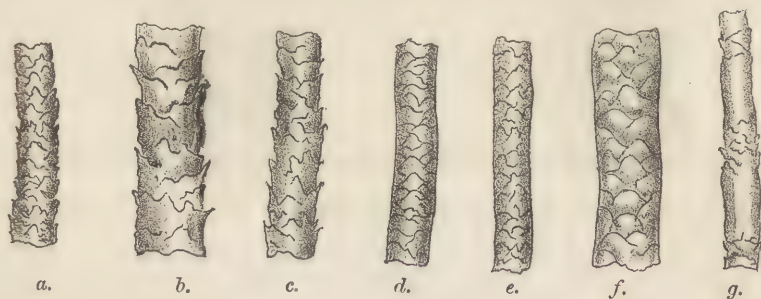


Fig. 8.—Microscopical appearance of various wool fibres.

- a*, Fine merino. *b*, Lincoln wool taken from the coarsest part of the fleece after treatment with caustic soda and washing with alcohol and water. *c*, Lincoln wool taken from the shoulders of the same fleece as *b*. *d*, Alpaca. *e*, Mohair. *f*, Coarse hair from Cheviot fleece. *g*, Kempy fibre.

solid rod-shaped substance, the surface of which is covered with broad scales, all projecting in the same direction, almost like the scales of a fish or serpent.

When the animal has been clipped for the first time, the fibre tapers to a blunt point, but after the second and subsequent clips, it terminates abruptly.

We owe to Dr. F. H. Bowman our knowledge of the internal structure of the wool fibre. According to this authority, it consists of a vast number of individual cells which taper towards each end to a finer point.

The central or medullary cells are generally somewhat larger than those immediately surrounding them ; and, in the case of black or coloured wool, contain the organic pigment to which the wool owes its colour. The outer, or epithelial, cells are flat, horny, shield-shaped discs, which overlap each other, as will be seen in Fig. 8 (especially in *b* and *c*). These cells can be made to stand out more prominently by treating the wool with sulphuric acid. Their presence also makes

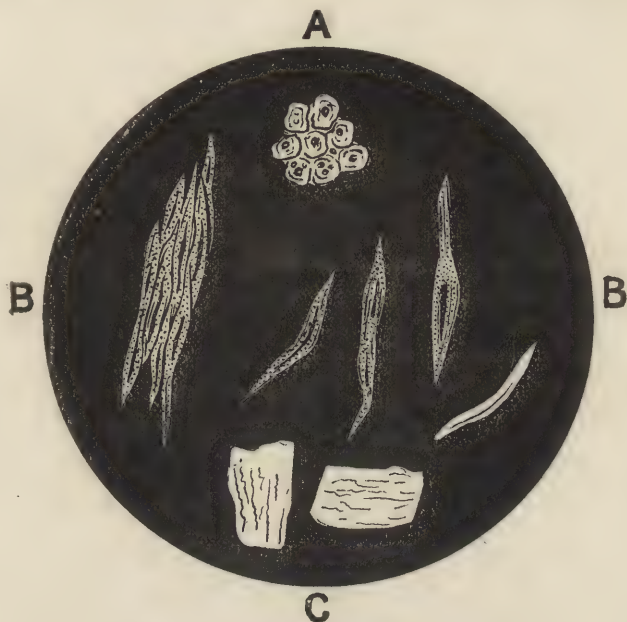


Fig. 9.—Individual cells of wool fibre.

A, Medullary cells ; B B, cells from cortical substance ; C, horny cells from the cuticle.

itself evident without the aid of a microscope ; for, if a single wool fibre or a hair is taken between the finger and thumb of each hand and drawn gently, the end nearest the root remains stationary while the other slips. This simple experiment is instructive as showing the behaviour of wool in the process of *milling*. In the “drawing” of wool for worsted yarns, as also in the carding and drawing for woollen yarns, the result of the operations is that about 50 per cent. of the fibres lie in one direction and 50 per cent. in the other.

If worsted or woollen fabrics are subjected to friction in the wet state, especially in presence of an alkali (soap or soap and soda), the

friction of the fibres against each other is greater in one direction than in the other, and the consequence is that the fabric contracts or "runs" or "felts," becoming at the same time thicker and assuming a denser appearance. The object of *milling* is to produce this effect. The process is used in the manufacture of flannels, broadcloths, tweeds, and other classes of woollen goods. As soap is generally used to accelerate its action, the colours used in dyeing the wool or the yarn for all but plain goods must be fast to soap, and should not run or bleed. In the dyeing of slubbing and yarn, this property of felting is a drawback, and careful treatment of the material is necessary in order to avoid its occurrence. In the production of felt from rabbit's fur, the fibres are specially treated with nitrate of mercury in order to make them felt well.

The number of cells seen in a transverse section of the wool fibre may exceed (according to Bowman) 1,500. In section the fibres are generally round or elliptical.

The length and diameter of the individual wool fibres varies considerably, not only according to the origin, but also in one and the same fleece. As stated above, the diameter is usually proportional to the length. The average length of the various classes of wool may be taken as varying between $1\frac{1}{2}$ and 7 inches, and the diameter from 0.004 to 0.0018 inch. The following interesting data are taken from Bowman's *Structure of the Wool Fibre* :—

Kind of Wool.	Breaking Strain in Grains.	Elasticity in Percentage of Length.	Diameter of Fibre in Decimals of an inch.
Leicester Wool,	502	0.284	0.00181
Southdown Wool,	86	0.268	0.00099
Australian Merino,	50	0.335	0.000517
Saxony	39	0.272	0.000338
Mohair,	586	0.299	0.00170
Alpaca,	149	0.242	0.000526

In the coarse qualities of wool, and especially in mohair, fibres are frequently met with which strike the eye by their characteristic ivory-white appearance. Under the microscope these fibres are seen to be void of internal structure, they have no felting or matting power, and in dyeing come out considerably lighter than the other fibres of the same wool. They are technically known as *kemps*, and, although they are usually eliminated to a great extent in the process of combing, those which remain are a source of annoyance to the spinner, manufacturer, and dyer alike. It does not always happen that the whole fibre is

kempy. It may be healthy up to a certain point and thence kempy to the end, or even kempy in the middle and healthy at both ends.

In their chemical composition, kemps do not appear to differ from the healthy fibres, and their different behaviour in dyeing must be due to the horny impenetrable nature of the fibre.

Physical Properties.—Wool is hygroscopic, and to a much greater extent than the vegetable fibres. When dried at 100° C. wool loses on an average 18·25 per cent. of moisture, and this is the amount officially allowed by the conditioning establishments on the Continent. But the amount of moisture held by the wool may be considerably less than or in excess of this figure according to the temperature and hygrometric condition of the atmosphere in which it has been kept. In fairness, therefore, to both buyer and seller, conditioning houses have been established in all the most important



Fig. 10.—Transverse section of wool fibre (Bowman).

worsted and woollen manufacturing centres of the Continent and, recently, also in Bradford, in which the wool is sampled and tested for the amount of hygroscopic moisture and oil which it contains. The *modus operandi* is similar to that used in conditioning silk (*q.v.*)

Wool dried at 100° assumes a harsh feel and its strength becomes considerably diminished. But if exposed to the air it soon takes up all its moisture again and resumes its original condition. According to Bowman, however, the water is present in two conditions:—1, as moisture, and 2, as water of hydration. The water of hydration driven off at 36° amounts to 8½ per cent., and the rest is given off at 100°. But according to this authority, the wool is chemically altered at this temperature. When exposed to temperatures above 110°, the wool

fibre begins to become affected, while at 130° a more or less complete-decomposition of the fibre sets in. This can be avoided, according to Persoz, by previously impregnating the material with a 10 per cent. solution of glycerin. After this treatment it can be exposed without alteration to a temperature of 130° to 140° .

At 100° , wool becomes plastic, and can be made to assume in this condition almost any shape which may be given to it, which shape is retained afterwards, if the material is allowed to cool in the same position. This plasticity of the wool fibre is of the greatest importance in the crabbing and hot finishing of piece goods and in the stretching of yarns. With horn, which is morphologically and chemically closely allied to wool, the property may be readily demonstrated by plunging a spatula of this material for a few minutes into boiling water. When taken out it is quite limp, and can be readily bent in any direction. If it is now bent double and plunged in this position into cold water, it retains the shape that has been given to it, and cannot be bent straight again while cold.

Chemical Properties of the Wool Fibre.—Chemically, the wool fibre differs from all others in its composition and properties. When it comes from the sheep's back, the fibre is in a very impure condition, being contaminated with a large amount of grease (yolk) and dried-up sweat (suint). These constituents will be dealt with below under wool-washing. When thoroughly cleansed the wool fibre is found to be composed of carbon, hydrogen, oxygen, nitrogen, and sulphur, but as these elements (especially the sulphur) are not present in constant proportions, it is not possible to assign to wool a definite chemical formula. It consists of keratine, a proteid substance, the constitution of which is little known, but which constitutes not only the wool fibre, but all horny tissues, such as horn, whalebone, feathers, &c.

The average composition of wool-keratine may be taken as—

Carbon,	50.00	per cent.
Nitrogen,	15-17	„
Hydrogen,	7.00	„
Sulphur,	2-4	„

the difference between the sum of these figures and 100, being oxygen. The amount of sulphur, which averages from 2 to 4 per cent., may even exceed these limits considerably. Thus wools have been examined which have contained as little as 0.8 per cent., while Bibra found in some red human hair which he examined no less than 8.23 per cent. The sulphur contained in wool seems to be of two kinds, one of which may be removed by prolonged treatment with alkali, while the other can not. By successive treatments with lime-water, water and hydrochloric acid, Chevreul succeeded in reducing the amount of sulphur in one case to 0.46 per cent. Wool dissolved in caustic soda and then treated with dilute acid gives off about 70 per cent. of the sulphur originally present as sulphuretted hydrogen.

The presence of sulphur in wool can be readily shown by heating the material in a diluted solution of lead oxide in caustic soda. The fibre soon turns brown and ultimately black, owing to the formation of lead sulphide. Advantage is taken of this reaction for readily distinguishing wool from other textile fibres, for the production of cheap (but injurious) hair-dyes, and for making imitation tortoise-shell from ordinary horn. On the other hand, the presence of sulphur in wool is not without its drawbacks, as will be seen from the following series of experiments carried out by Rawson.*

The colouring matters taken were the following:—Naphthol yellow, tartrazin, Manchester yellow, brilliant green, safranine, magenta, rhodamine, and night blue. The only natural colouring matter experimented upon was indigo, which was dyed in the form of indigo-sulphonic acid. Some of these colouring matters were dyed in a neutral bath, and others with addition of sulphuric acid. The experiments were made in series of four. In the first place the water used was free from lead, in the second $\frac{1}{3}$ grn. of lead per gallon was added, in the third $\frac{2}{3}$ grn., and in the fourth 1 grn. per gallon. Wherever sulphuric acid is used in dyeing the colour is not affected by lead, but shades dyed in a neutral bath are rendered duller in proportion to the amount of lead present in solution. Wool treated neutral and with acid, without addition of colouring matter, behaved in a similar manner. In a neutral bath containing lead the wool was dyed a drab shade, but with addition of a small quantity of sulphuric acid ($2\frac{1}{2}$ per cent. on the weight of the wool) it remained white. In the case of rhodamine, one of the brightest of all colouring matters, 5 per cent. of alum was used in the dye-bath, and the shade was almost, but not entirely, unaffected by the presence of lead. In the case of night blue, the colour was dissolved in acetic acid, but the shade was affected in a similar manner to those dyed neutral. It is true that the amount of acetic acid present in the dye-bath would be exceedingly small, and the effect of a larger amount was not tried. The saddening effect is apparently caused by the sulphur naturally present in the wool combining with the lead, and forming sulphide of lead. But the formation of sulphide of lead on the fibre does not take place in the presence of sulphuric acid.

In mordanting wool with stannous chloride, the material sometimes blackens, presumably through the formation of stannous sulphide. A similar reaction sometimes takes place, according to Hummel, in the formation of black specks in dyeing cochineal scarlets on woollen cloth.

The ash of cleansed wool amounts, as a rule, to less than 1 per cent. by weight of the original material, and about three-quarters of it is soluble in water. The following analysis, by W. H. Wood, of

* *Journ. Soc. Dyers and Col.*, 1889, p. 161.

the ash of Lincoln wool may be taken, according to Bowman, as typical:—

Potassium oxide, K_2O ,	31.1 per cent.
Sodium „, Na_2O ,	8.2 „
Calcium „, CaO ,	16.9 „
Alumina, Al_2O_3 ,	}	12.3 „
Ferric oxide, Fe_2O_3 ,		
Silica, SiO_2 ,	5.8 „
Sulphuric acid, $S O_3$,	20.5 „
Carbonic acid, $C O_2$,	4.2 „
Phosphoric acid,	trace.
Chlorine,	trace.

99.0

The ash of a scoured flannel was found by Fürstenhagen and Appleyard to be alkaline.* The alkalinity was due to

Lime,	0.094 per cent. calculated as CaO .
Potash and soda,	0.224 „ „ as K_2O .

The substance of the wool fibre is a horny, transparent, or translucent mass which is not affected by the ordinary solvents. When boiled, however, for a length of time with water, the lustre of the fibre suffers, while, at the same time, traces of ammonia and sulphuretted hydrogen are given off. Heated with water under pressure to 130° , the fibre is so altered that it may be rubbed to a fine powder after drying. By this means it is possible to destroy or carbonise wool in presence of silk and cotton. At still higher temperatures (150° to 200°) the wool is completely dissolved.

Behaviour towards Acids.—Dilute acids have little appreciable effect on wool, although they are absorbed and retained by the fibre with great tenacity. The amount of sulphuric acid absorbed from boiling solutions, using 500 cc. of liquid to 5 grammes of wool, was found by Fürstenhagen and Appleyard† to be as follows:—

Amount of Acid employed.	Acid left in solution.	Acid absorbed.	Indicator.
2½ per cent.	0.38 per cent.	2.12 per cent.	Methylorange.
5 „	2.17 „	2.83 „	„
10 „	6.37 „	3.63 „	„
20 „	15.87 „	4.13 „	„
40 „	35.18 „	4.82 „	„

The acid thus absorbed cannot be readily extracted by boiling.

* *Journ. Soc. Dyers and Col.*, 1888, p. 104.

† *Ib.*, 1888, p. 104.

Thus wool which had been mordanted with 5 per cent. of sulphuric acid gave up to distilled water when boiled for an hour (500 cc. water to 5 grammes wool), the following amounts:—

First boiling,	0·84 per cent.
Second „	0·34 „
Third „	0·08 „
								<hr/>
								1·26 „

Further treatments continue to extract small quantities of free acid, but a not inconsiderable portion appears to be permanently absorbed or neutralised by the fibre. It is a remarkable fact that wool, which has been boiled with—say 10 per cent.—sulphuric acid, and then extracted repeatedly with water until the reaction is neutral, can be dyed in a neutral bath with the acid colours, which otherwise require a considerable amount of acid in the dye-bath.

Sulphurous acid is also absorbed and retained tenaciously by the fibre; and wool which has been stoved for the purpose of bleaching must be treated before printing with chloride of lime or peroxide of hydrogen, in order to convert the sulphurous into sulphuric acid. If this is omitted, the sulphurous acid retained by the wool will either prevent the fixation of certain colouring matters or cause them to fade after printing, owing to its reducing action.

From dilute aqueous solution, *hydrochloric acid* is absorbed like sulphuric acid. *Tartar* is decomposed by wool, according to Bolley, neutral tartrate being left in solution, while tartaric acid is retained by the fibre. Wool boiled for an hour in a solution of 10 per cent. tartar left, according to Fürstenhagen and Appleyard, 5·6 per cent. in solution and absorbed 4·4 per cent. These figures do not show to what extent a decomposition of the salt has taken place, but merely indicate the analytical results obtained with caustic potash and phenolphthaleïn.

Dilute *nitric acid* when applied at boiling temperature is liable to turn the wool yellow. The colour thus produced is due to the formation of xanthoproteic acid. But if the strength does not exceed 3° to 4° Tw., the formation of this compound takes place very slowly. Acid of this strength is frequently used by job-dyers, and, in shoddy dyeing, for “stripping” colours.

According to Richard,* wool treated with nitrous acid becomes yellow, and is at the same time diazotised. If subsequently washed and passed through alkaline solutions of phenols, various colours (azodyes?) are produced on the fibre, according to the nature of the phenol employed.

Concentrated mineral acids completely destroy and dissolve the wool fibre. When dissolved in strong sulphuric acid, wool yields a product which has the property of forming insoluble precipitates (lakes) with

* *Journ. Soc. Dyers and Col.*, 1888, p. 154.

the acid colours. A similar compound is produced when wool is dissolved in strong hydrochloric acid; but in this case the action is slower. Nitric acid dissolves wool with copious evolution of nitrous fumes. The solution has an intense yellow colour; although sulphur is a constituent of wool, it is curious that this solution gives no precipitate with barium chloride.

Behaviour towards Alkalies.—Although proof against the action of even moderately diluted acids, wool is very easily acted upon by alkalies. The most powerful in this respect are the caustic alkalies and the hydrates of the alkaline earths. Their action varies, however, greatly according to temperature and strength of solution. At 0° the action of even concentrated caustic alkalies on wool is only slight, but as the temperature increases, their action becomes more and more intense, until, at the boiling temperature, wool can be completely dissolved by prolonged treatment in a solution containing less than one per cent. of caustic soda calculated on the weight of the material.

The decomposition products formed by dissolving wool in caustic soda or barium hydrate comprise, in addition to ammonia and sulphuretted hydrogen, a number of organic compounds—chiefly acids or amidoacids. The most interesting of these compounds is that known as *lanuginic acid*.* It may be prepared by dissolving wool in boiling barium hydrate solution, removing the barium by means of carbonic acid, filtering, precipitating the lanuginic acid with lead acetate and decomposing the washed lead salt in a large volume of water with sulphuretted hydrogen. The filtrate evaporated to dryness yields the product in the form of a brownish-yellow mass, which on grinding yields a cream-coloured powder easily soluble in hot water. Its aqueous solution precipitates the acid and basic colours forming intensely coloured lakes. With tannic acid, bichromate of potash, and the acetates of alumina, iron, chromium, and copper, it also forms precipitates. At 100° lanuginic acid becomes soft and plastic, and this property is shown more strikingly by its coloured lakes, most of which melt at this temperature. At higher temperatures it swells up, turns brown, and gives off a smell similar to that of burning wool. The average of two analyses showed lanuginic acid to possess the following percentage composition:—

Carbon,	41·61 per cent.
Hydrogen,	7·31 "
Nitrogen,	16·26 "
Sulphur,	3·35 "
Oxygen,	31·47 "
<hr/>	
100·00	

The property of lanuginic acid to precipitate the colouring matters

* *Journ. Soc. Dyers and Col.*, 1889, p. 71.

and mordants is of importance as showing that it is possible to produce from wool a substance soluble in water, which behaves towards the dyes and mordants in a manner similar to the fibre itself. Products having similar properties are obtained by disintegrating wool with strong mineral acids or with water at high temperatures. If we now assume that lanuginic acid is a constituent of the fibre which has been rendered soluble by any one of these agencies (just as albumen is rendered insoluble by the action of heat without changing its chemical composition), the above facts would go a long way towards establishing a purely chemical theory of dyeing, in the case of wool at least.

Wool has the property of absorbing caustic alkalis from dilute aqueous solution, as it does acids, but it does not retain the alkali so tenaciously as it does acids.

Alkaline carbonates (sodium and potassium carbonates) exercise a destructive action on wool, although to a far less degree than the caustic alkalis. In dilute aqueous solution and at moderate temperatures they are often used along with soap for scouring wool and in milling. As a rule, no injurious effect is observed under these conditions, but it is well to bear in mind that their deteriorating effect increases with the strength of the solution, and more especially with the temperature; in comparatively dilute boiling solution of sodium carbonate, wool is readily tendered, and by prolonged action it is completely disintegrated.

The milder alkalis, like soap, borax, phosphate of soda, &c., have much less action on the wool fibre. The use of these substances is resorted to when it is necessary to boil the wool in an alkaline bath, as, for instance, in the dyeing of alkali blue. Ammonia and ammonium carbonate are also comparatively uninjurious.

Behaviour towards Oxidising Agents.—Boiled in a solution of permanganate of potash, wool rapidly turns brown, and the fibre is easily tendered by the consequent oxidation. So-called "overchromed" wool, *i.e.*, wool which has been mordanted with an excessive amount of bichromate of potash and sulphuric acid, also appears to have suffered through oxidation; when it has once undergone this change it can no longer be dyed black in logwood.

Wool greedily absorbs moist chlorine gas and is thereby ultimately destroyed; dry chlorine does not act.* From dilute aqueous solution it also absorbs chlorine and appears to act upon it chemically without the fibre itself undergoing any material change in appearance.

By the prolonged action of moist chlorine, wool is turned yellow and becomes converted into a translucent sticky substance, while at the same time large amounts of hydrochloric acid are given off. The substance formed has not yet been prepared in a pure state, but it has been found to resemble lanuginic acid in its property of precipitating colouring matters from aqueous solution. That modification of sulphur which blackens with alkaline lead solution is not destroyed

* *Journ. Soc. Dyers and Col.*, 1892, p. 41.

in the ordinary chlorinating process used in printing, and only disappears when the action of the chlorine has proceeded sufficiently far as to partly destroy the fibre.

By hypochlorous acid, wool is turned yellow much more readily than by free chlorine. The yellow colour can be removed by sulphurous acid, but reappears on steaming.

By careful treatment, wool can be made to absorb, according to Witt,* as much as 33 per cent. of its weight of chlorine. Chlorinated wool resembles silk in many of its properties; it has an increased lustre and a "scroop" feel. At the same time it has become harsh and has lost its property of felting. It dissolves readily in ammonia with evolution of nitrogen gas. Another interesting change which chlorinating effects in wool is an increased affinity for certain colouring matters.† Practical use is made of this in preparing delaines for printing by running the pieces for some time in a dilute solution of bleaching powder acidulated with hydrochloric acid. The advantages of this treatment are especially marked in dyeing or printing with the indulines and naphthol black.

Behaviour towards Solutions of Metallic Salts.—Solutions of salts, which are neutral to litmus, such as sodium chloride, sodium sulphate, calcium chloride, &c., are quite without action on the wool fibre. Wool boiled in solutions of sodium chloride and calcium chloride absorbs only traces of these salts. But when boiled for some time in solutions of metallic salts, like aluminium sulphate, copperas, chrome alum, &c., which are acid to litmus, considerable quantities of the salt are taken up by the fibre. This takes place in the mordanting of wool, previous to dyeing it with adjective colours, and an exact knowledge of the chemical changes which take place would, therefore, be of considerable interest. A prevalent opinion is that when wool is boiled with aluminium sulphate, for instance, the salt is decomposed by the fibre in such a manner that aluminium hydrate and sulphuric acid are formed, of which the former is assimilated by the fibre, while the latter remains in solution. Others again assume that an insoluble basic sulphate of alumina is formed on or in the fibre. The following quantitative determinations, carried out by Fürstenhagen and Appleyard ‡ on this question are of interest. The first column gives the amount of potash alum employed as mordant in percentages of the weight of the wool; the second and third columns give the amounts of sulphuric acid left in solution and absorbed by the fibre respectively, calculated in percentages on the amount of alum employed. (Potash alum contains 25.4 per cent. of sulphuric acid as SO_3):—

* *Chem. Techn. d. Gespinnstfasern*, p. 91.

† The same property is imparted to wool by treatment with permanganate of potash.

‡ *Journ. Soc. Dyers and Co.*, 1888, *r.*, 165.

Alum Employed.	SO ₃ in Solution.	S O ₃ Absorbed.
5 per cent.	0·0 per cent.	25·4 per cent.
10 ,,	3·3 ,,	22·1 ,,
15 ,,	10·8 ,,	14·6 ,,
20 ,,	14·4 ,,	11·0 ,,

It is thus seen that wool mordanted with 5 per cent. of alum left only a trace of *free* sulphuric acid in solution. Now it has already been shown that wool possesses a considerable affinity for both acids and bases, and, in its whole behaviour, it evinces the properties of an amidoacid, that is, of a substance possessing simultaneously basic and acid properties. This would explain in a satisfactory manner the fixation of both the acid and basic constituents of the alum, but in what form these are fixed still remains a matter of conjecture. It is not improbable that the phenomenon is due to actual chemical combination with the fibre or with certain constituents of the latter; just as lead or mercury, when absorbed by the system, enter into chemical combination with the albuminoids in the various organs. That a hydrate is not formed is shown pretty conclusively in mordanting wool with copper salts. The fibre assumes a green colour, but copper hydrate when boiled is at once dehydrated and transformed into black copper oxide. If copper hydrate had been formed, the fibre would be black, whereas it is green, and remains so even after prolonged boiling.

The behaviour of wool towards bichromate of potash in mordanting will be found under the heading "bichromates" among the mordants.

Cold solutions of *tannic acid* have little effect on the fibre, but when boiled in a solution of a tannin (like myrabolans, for instance) the wool appears to absorb tannic acid, and its properties become altered. If chromed wool is boiled in a decoction of logwood to which myrabolans have been added, it is said that it is impossible to dye it black.

Behaviour towards Colouring Matters.—Wool, of all textile fibres, exhibits the most powerful affinity for the colouring matters. It combines directly with all the substantive dyes, and can be readily dyed with them. Its affinity for these is generally greater than that of silk; in other words, the colours produced on wool resist the action of boiling water or of soap better than those on silk. Thus, if wool and silk are dyed the same shade with naphthol yellow or indigo extract and then boiled with water, the colour is extracted from the silk much more rapidly than it is from the wool. There are some exceptions to this rule, and on these facts is based the principle of dyeing the wool and silk, in mixed goods manufactured from these

two fibres, two entirely different shades in one bath. As shown by Hirsch,* wool also evinces a strong affinity towards certain substances, like the naphthol sulphonic acids, which are not dyes in themselves, but are capable of forming dyes by subsequent treatment. Thus wool boiled in acid solution with 1 to 2 per cent. beta-naphthol disulphonic acid, R, became orange when passed into a solution of diazotoluene after the addition of ammonia. In a similar manner naphthol green may be produced on the fibre by boiling in naphthol monosulphonic acid, passing through an acidulated bath of nitrite of soda and then into a hot copperas solution.

For some adjective dyes, such as the insoluble red dyewoods and catechu, wool also exhibits a direct affinity. Others, like alizarin, which are used in dyeing in the form of pastes containing the colouring matter in a very finely divided state, are absorbed mechanically and fixed loosely by the fibre.

The various qualities of wool behave differently in dyeing, the finer qualities generally requiring more dyestuff to produce a given shade than the coarser ones. The amount of dyestuff required also varies according as the wool is dyed as loose wool, slubbing, yarn, or in the piece; the former requires most, the latter least dyestuff.

Certain kinds of wool, like mohair, are sometimes very difficult to dye; they appear to take up only a very small proportion of the dyestuff, in spite of prolonged boiling. In these cases a short steaming is generally found to be effective in overcoming the difficulty. In some cases this peculiar action of steam on wool may be a drawback (see *crabbing*, p. 134).

SILK (GER., *Seide*; FR., *Soie*).

Silk is the fibrous substance which is excreted by the silkworm, and with which it envelopes itself in a *cocoon* when it enters into the chrysalis stage of its existence.

The numerous kinds of silk which come into commerce may be conveniently classed as *artificially* reared, and *wild* silks. The former are by far the most important. The principal species of silkworm is the *Bombyx mori*, or mulberry silkworm, which is reared in China, Japan, India, Italy, the South of France, Greece, and The Levant. The worms are reared in Asia in the open air, but in Europe this is done in specially constructed buildings or sheds, which the French call *magnaneries*. Here the eggs are laid out on shelves covered with white paper, and the temperature of the room is gradually raised during about 12 days from 18° to 25°. Under these conditions the eggs are hatched. The caterpillars are taken into a more spacious room, where they are fed on the leaves of the white mulberry (*Morus*

* *Journ. Soc. Dyers and Col.*, 1889, p. 115.

alba). The caterpillars evince an enormous appetite, and grow rapidly to their maximum size in from 30 to 33 days, changing their skin every 4 to 6 days. At this stage their movements become slow, and they cease to take nourishment. They are allowed to creep into birch twigs, or bundles of broom or heather placed in their vicinity, where they spin themselves into cocoons.

The spinning lasts about 3 days, but in order to be sure that all the worms have finished spinning, 5 days are generally allowed to elapse before the cocoons are collected and killed.

The substance from which the fibre is produced is found in the silk worm before spinning in the form of a clear, colourless, sticky liquid, which is secreted from two glands situated symmetrically on either side of the body, and communicating with a capillary orifice in the head (the spinneret). According to Duseigneur, a section of the silk gland shows the presence of two liquids, an outer one, which in natural yellow silk is coloured yellow, and which constitutes from 20 to 25 per cent. of the whole, and an inner one which is always colourless. These quantities correspond with the relative amounts of sericine and fibroine found in the raw silk.

On coming in contact with the air, the silk liquid solidifies, forming a uniform double fibre which in some places may be seen separated into two fibres.

After the cocoons have been collected, and some of the finest sorted out for breeding, the rest are killed, either by exposing them in stoves to a temperature of 60° to 75° for three hours, or by steaming them for about ten minutes. In this state they are brought into the market.

The first mechanical operation to which the cocoons are subjected, after being sorted into different qualities, is that of *reeling*. The contrivances used for this purpose differ somewhat in their construction. The best results are produced, according to Wardle, by means of the Italian tavelette devised by Keller, and shown in Fig. 13.

It consists of an iron stand, A, 12 inches in height. B represents the cocoon and its thread, placed so as to show the position of the silk on the instrument. C is the *filière*, a porcelain disc, pierced in the centre and concave on the lower side.



Fig. 11.—Caterpillar, cocoon, and silk on moth mulberry twig.

The threads of four or more cocoons pass through it and form a compound thread of "raw silk." D is the *croissure* or crossing of the raw-silk thread six or more times round itself. The object of this is to straighten and remove kinks and irregularities in the thread. E E are pulleys, the drums of which are formed of thin glass rods. F F are porcelain eyelets or guiders attached to a brass frame which also supports the pulleys.

A number of cocoons are thrown into a basin, which contains water heated by gas or steam to about 60° C. The fibres of from 4 to 18 individual cocoons are collected by the operator and pass through the eye of the *filière*, thence following the same course as

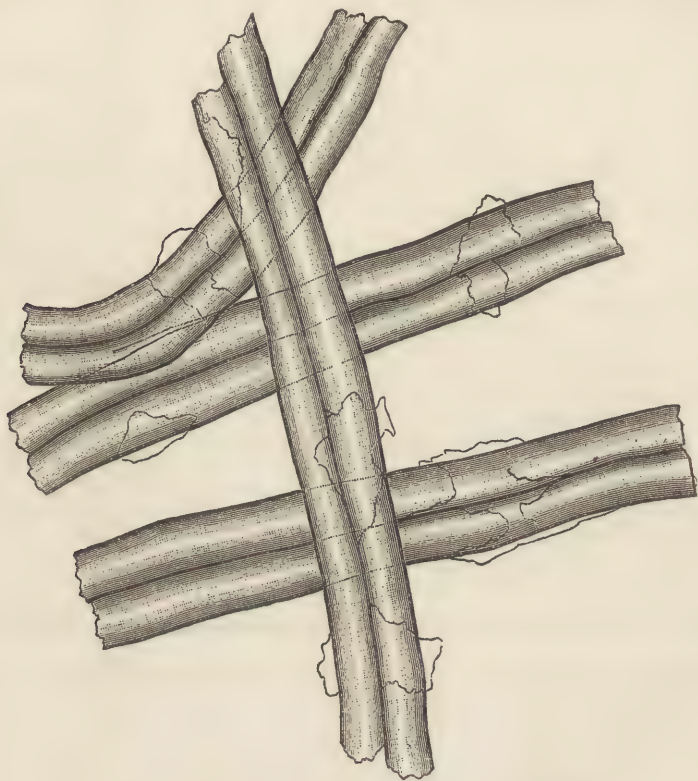


Fig. 12.—Microscopical appearance of silk fibre.

shown in detail in Fig. 13, and ultimately through the guides, F, on to a reel. The operator always has a number of ends of fresh cocoons ready, so that as soon as one has come to an end, it is at once replaced by a fresh one. By the action of the hot water in the vessel, some of the gum or silk-glue becomes dissolved and causes the individual fibres to cohere and form one thread, which varies in thickness according to the number of cocoons constituting it.

A single fibre is known as *grège*. By combining a number of *grège* fibres and using additional twist, *organzine*, or warp silk, is produced,

whilst by using a smaller number of fibres and adding less twist *trame*, or weft silk, is obtained.

The silk reeled direct from the cocoons is the most valuable quality, and constitutes the *raw silk* or *net silk* of commerce. The outer portions of the cocoon, which consist of a loose tangle of threads, are used in the manufacture of *floret silk*; the innermost layer which envelopes the chrysalis, also the pierced cocoons, double cocoons, and those which have been spoilt in steaming, constitute the inferior qualities, and are used for the manufacture of *spun silk*. For this purpose they are fermented with water, boiled with soda, washed and dried; after being torn to shreds, the material is combed, carded, and spun on machinery similar to that used for worsted. *Chappe silk* is produced in a similar manner, but without previously boiling the material.

Counts.—In thrown or net silk, the counts indicate the weight per hank of 1,000 yards. For spun silk, the counts are the same as for cotton (*q.v.*)

Structure of the Silk Fibre.—As it comes into the market raw silk appears in the form of a more or less coarse uniform fibre, generally of a light creamy white, but sometimes of a bright yellow colour (especially in Italian silk). It has a harsh feel and little lustre. As has already been pointed out, these fibres are made up from the individual fibres of from 4 to 18 cocoons. The fibre drawn from a single cocoon varies in length from 350 to 1,250 metres, and has an average diameter of about 0.018 mm. The diameter is greatest at the outside and diminishes towards the interior of the cocoon.

After removing the silk-gum, by boiling with soap, the silk separates into its individual fibres, and is, in this condition, distinguished by its

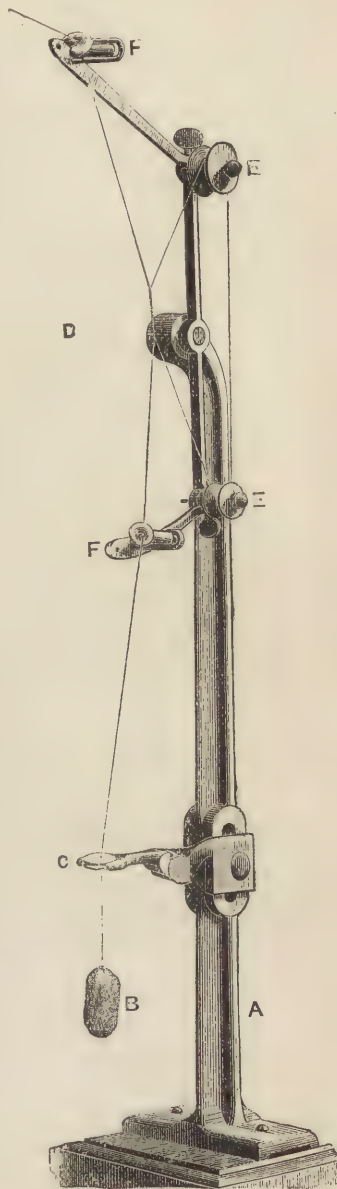


Fig. 13.—Keller's tavelette or silk-reeling machine.

beautiful lustre, fineness, strength, and elasticity. Under the microscope it presents the appearance of a structureless, transparent, rod-shaped fibre.

Physical Properties.—Like wool, silk is a very hygroscopic substance. It may be made to absorb up to 30 per cent. of its weight of moisture without feeling damp. This fact, coupled with the high price of silk, renders it necessary for the buyer on the one hand and the seller on the other to know exactly the "condition" of the silk in which a transaction is made. This is done in all the more important silk centres, like Lyons, St. Etienne, Paris, Crefeld, Milan, Zürich, London, &c., officially in the so-called conditioning houses.*

Up to the year 1841 the method employed for conditioning consisted in exposing the selected samples on trays for 24 hours to the air in a room heated to from 20° to 25° C., and ascertaining how much they lost or gained in weight. The method did not give satisfactory results, owing to the variations in the hygrometric condition of the atmosphere. In 1841, Talabot introduced the method in use at the present time (with Persoz's improvement of drying in a current of air) of determining the absolute weight of the silk dried at 110° to 120° C. The whole bulk of the silk to be conditioned is weighed, and samples are taken out from various parts weighing in the aggregate about 1,500 grms. This sample is divided into three lots. Two of these are weighed to within 0.50 grm., and dried in a specially constructed apparatus in a current of air heated from 110° to 120° until the weight is constant. If the results are within half a per cent. of each other, the mean is taken; if not, the third lot is treated in a similar manner and the mean of the three is taken. The condition of the bulk is then arrived at by adding to its absolute weight, which is calculated from the loss in weight of the samples, the legal quantity of moisture, viz., 11 per cent.

Silk has a specific gravity of 1.367. It is a bad conductor of electricity and easily becomes electrified by friction. This is a drawback to the manufacturer, but it can be overcome to a great extent by keeping the atmosphere of the room moist.

A silk fibre can be stretched one-seventh to one-fifth of its length without breaking. When treated with aqueous solutions of certain metallic salts, it may contract 0.7 per cent. in length. Raw silk possesses greater elasticity and greater tensile strength than "discharged" silk. By discharging the gum the strength decreases by 30 per cent., the elasticity by 45 per cent. When wetted, silk possesses less tensile strength, but greater elasticity than dry silk.

Chemical Composition and Properties of Silk.—Raw silk is not a uniform substance, but consists of two substances, viz., the fibre proper (fibroïne); and the external covering, which is known as silk-

* The first conditioning establishment for silk was founded in Turin in 1750 by order of the King of Sardinia. In 1779 one was founded in Lyons.

gum or silk-glue (sericine). The silk-gum is soluble in boiling water or dilute soap solution, while the latter is not. The silk-gum constitutes 20 to 25 per cent. of the raw silk.

The silk fibre, freed from all impurities by treatment with water at 133°, then with alcohol, and lastly with ether, constitutes what is chemically known as *fibroïne*. Mulberry silk does not appear to vary much in its chemical composition, which corresponds to the formula $C_{15}H_{23}N_5O_6$. It exhibits the properties of an amidoacid.

Prolonged boiling with water slightly weakens the fibre; boiling temperatures are, therefore, avoided as much as possible in dyeing and discharging. The action is, however, not very noticeable. Silk heated with water to 130° for 3 hours loses somewhat in tensile strength, whilst wool subjected to the same treatment is completely disintegrated.* Commercial "boiled off" silk contains, on an average, 0.7 to 1 per cent. of ash, consisting principally of lime, magnesia, alumina, and iron.

Behaviour towards Acids.—Silk is rapidly attacked and dissolved by concentrated mineral acids. Concentrated hydrochloric acid is capable of dissolving more than its own weight of silk. When diluted with water and neutralised, a flocculent precipitate is formed from this solution. Nitric acid dissolves silk, forming a yellow solution.

Silk absorbs acids from dilute aqueous solution like wool does, and retains them tenaciously. The lustre of the fibre is at the same time increased, and the silk acquires a peculiar feel, emitting when compressed in bulk a peculiar crackling sound (*scroop silk*; Fr., *craquant*). This property is frequently desired by the purchaser. In order to produce it, the silk is worked, after dyeing, for a short time in a dilute solution of acetic, tartaric, or sulphuric acid (brightening), and then dried without washing. Tartaric acid gives the best results, but it is the most expensive. The scroop feel produced by acetic acid disappears after a time, owing to the evaporation of the acid.

According to Fürstenhagen and Appleyard, silk treated for an hour in a solution containing 22.5 per cent. of tartaric acid (calculated on the weight of the silk) absorbed 2.5 per cent. Silk boiled for one hour in a solution containing 20 per cent. of sulphuric acid (calculated on the weight of the fibre) retained 1.5 per cent. According to Lidow, glacial acetic acid, as well as molten citric and oxalic acids at elevated temperatures, dissolve silk rapidly and completely. Hot dilute nitric acid turns the fibre yellow, presumably through the formation of xanthoproteic acid, and was formerly used for dyeing yellow.

Behaviour towards Alkalies.—At 0°, caustic alkalies have little action on the silk fibre, even if used in a sufficient degree of concentration to mercerise cotton. Advantage is taken of this in the production of

* *Journ. Soc. Dyers and Col.*, 1891, p. 58.

puckered effects in silk material containing cotton binding threads at regular intervals in the warp and weft. Hot solutions of caustic alkalies, however, dissolve silk completely, though not so readily as they do wool. Numerous decomposition products are found in the solution, amongst which one especially—viz., *sericinic acid*, is of interest, as showing similar properties towards the colouring matters to those of the lanuginic acid obtained from wool. In very dilute aqueous solution the caustic alkalies have little injurious effect on the fibre, and have been employed for discharging.

Ammonia has little action, even when applied hot. Alkaline carbonates (potassium and sodium carbonates) act like the caustic alkalies, but much less energetically.

Of the milder alkalies, the soaps may be specially mentioned as having little or no injurious effect on the silk fibre. They are used largely in ungumming or discharging, and in various processes of dyeing. *Borax* is similar in this respect. Prolonged action of *lime water* destroys the lustre and renders the fibre brittle.

Behaviour towards Oxidising Agents.—*Bichromate of potash* turns silk yellow, and by prolonged boiling a light olive; it is not suitable as a mordant. A strong solution of *chromic acid* rapidly destroys and dissolves the fibre.

Permanganate of potash turns the fibre brown and, if used in excess, rots it. A subsequent treatment with bisulphite of soda or sulphurous acids bleaches the fibre.

Chlorine and the *hypochlorites*, if used strong, attack the fibre and destroy it; but, if used in very dilute solution, they increase its affinity for certain colouring matters, but not to the same extent as is the case with wool.

Behaviour towards Metallic Salts.—In its behaviour towards metallic salts, like those of tin, aluminium, and iron, silk resembles wool. If soaked in cold and not too dilute solutions of these salts, an absorption takes place, which is due, as generally supposed, to the formation of a metallic hydrate, or of an insoluble basic salt on and in the substance of the fibre. Thus, if silk is steeped over night in a solution of basic ferric sulphate, wrung and washed, it assumes a yellow to yellow-brown colour, according to the strength of the solution employed. The phenomenon which plays a most important rôle in the mordanting and weighting of silk still requires a satisfactory explanation. It is a remarkable fact that silk which has been weighted with stannic chloride or ferric salts and not thoroughly washed out, is completely rotted if exposed to light.

A concentrated solution of zinc chloride (140° Tw.) rapidly dissolves silk to a thick sticky liquid, which can be diluted with acidulated water without the formation of a precipitate. By subjecting this solution to dialysis, the acid and zinc chloride are removed, leaving behind an aqueous solution of silk, which, when evaporated, leaves a brittle glass-

like substance insoluble in water. If the solution in zinc chloride is diluted with water alone and not with acidulated water, a flocculent precipitate is obtained, which can be freed from the chloride of zinc by washing. A solution of this precipitate in ammonia has been used for coating vegetable fibres with silk.

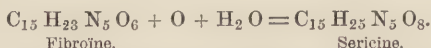
Silk is soluble in Schweitzer's reagent (solution of copper hydrate in ammonia), and also in a solution of nickel hydrate in ammonia. A solution prepared by dissolving 16 grms. copper sulphate in 140 to 160 cc. of water, then adding 8 to 10 grms. glycerin and, subsequently, caustic soda solution until the precipitate which forms just redissolves, is said to dissolve silk readily without affecting wool or cotton.*

Tannic acid and *sugar* are also absorbed by silk, and are used in weighting.

Behaviour towards Colouring Matters.—In its behaviour towards the colouring matters silk resembles wool; but the affinity is, generally speaking, less. This has already been referred to under wool. Although the matter has not yet been sufficiently investigated, it seems probable that the dyeing of silk is due principally to chemical action.

Silk-gum or *silk-glue*, the substance which envelops† the silk fibre proper in its raw state, consists chemically of a substance called *sericine*, which in its composition is closely allied to fibroïne. The chemical formula ascribed to purified sericine is $C_{15}H_{25}N_5O_8$. It forms a transparent, glue-like mass, which swells up and dissolves in hot water. Water containing as little as 1 per cent. of sericine gelatinises on cooling; prolonged boiling, or the addition of small quantities of nitric or acetic acid or caustic potash, prevent the gelatinising. Sericine is precipitated from its aqueous solution by alcohol, tannin, and the salts of most of the heavy metals. When boiled with dilute sulphuric acid or with barium hydrate, sericine is decomposed, yielding products similar to those formed from fibroïne.

The similarity in the composition of fibroïne and sericine has led to the supposition that the sericine is formed at the expense of the fibroïne as it leaves the spinneret of the silkworm by the absorption of oxygen and water, thus—



This theory is partly confirmed by the fact that if moist fibroïne is exposed for some time to the air, it becomes partially soluble in boiling water. Besides, the silk reservoirs contained in the worm are found to contain almost pure fibroïne, and very little matter soluble in water.

The sericine of raw silk contains, as a rule, small quantities of waxy,

* Löwe, *Jahresberichte*, 1876.

† According to M. Moyret (*Mon. de la Teinture*, 1891, p. 324), the sericine obtained by the action of various solvents on raw silk does not exist as such on this fibre, but consists of products which have become chemically altered in the process of ungumming, just as glue does not exist as such in the substances from which it is prepared (hide, bones, &c.)

fatty, and resinous matters, and in the case of yellow silk, a natural yellow colouring matter. According to Dubois,* the colouring matter of yellow silk is not a uniform substance, but contains :—

(1.) A golden-yellow colouring principle, soluble in solutions of potassium carbonate, from which it is precipitated by excess of acetic acid in brilliant flakes.

(2.) Various crystals of a yellow colour.

(3.) A lemon-yellow amorphous colouring matter.

(4.) Lemon-yellow octahedral crystals, similar to those of sulphur.

(5.) A dark bluish-green pigment, in very small quantities.

The same authority expresses the opinion that the yellow colouring matter of silk is analogous to, if not identical with, carotine.

WILD SILKS.

Of the so-called wild silks that known as *Tussur* (Tussah or Tasar) is the most important. It is imported into this country from India and

China; and, although formerly comparatively little known, is now used in large quantities principally in the manufacture of artificial sealskins.



Fig. 14.—Microscopical appearance of Tussur silk.

The Indian Tussur is the product of the *Antheraea mylitta*, while the Chinese Tussur is the fibre of another species of the same genus, viz., *Antheraea pernyi*, both belonging to the family *Saturniidae*. They do not appear to differ essentially from each other either in their physical or chemical properties.

Tussur silk comes into the market in the reeled state, but in much larger quantities as spun silk. It always has a brown colour which is difficult to remove. Tussur silk is much stiffer than ordinary silk and, principally on this account, is more suitable than the latter for the manufacture of pile fabrics. The diameter of the fibres is also considerably greater; while mulberry silk has an average diameter of 0.018 mm., the fibre of Tussur silk averages 0.052 mm. The raw Tussur appears under the microscope to consist of a flat double fibre. Each of these individual fibres can be split up by suitable treatment into 6 to 8 fibrillæ.

When seen in those parts where a twist in the fibre is prominent, it looks not unlike a cotton fibre, although differing from it in the high lustre and greater transparency. The surface marking of the fibres.

**Comptes rend.*, 1890.

consists principally of grooved lines, like the flutings of a column, and are evidently the result of the rising above the general surface of the fibre (before consolidation of the gum) of the small fibrillæ, of which every strand of the fibre is composed. The ribbon-like structure of the fibre gives it a peculiar appearance of unevenness in diameter, which thus appears to vary from $\frac{1}{500}$ to $\frac{1}{8000}$ of an inch.

Raw Tussur silk contains, as a rule, a high percentage of ash. In a sample of reeled Tussur (probably Chinese) Bastow and Appleyard* found 5.34 per cent. of ash calculated on the weight of the fibre dried at 100°. A quantitative analysis of the ash showed it to consist of—

Soda (Na_2O),	12.45 per cent.
Potash (K_2O),	31.68 „
Alumina (Al_2O_3),	1.46 „
Lime (CaO),	13.32 „
Magnesia (MgO),	2.56 „
Phosphoric acid (P_2O_5),	6.90 „
Carbonic acid (CO_2),	11.14 „
Silica (SiO_2),	9.79 „
Hydrochloric acid (HCl),	2.89 „
Sulphuric acid (SO_3),	8.16 „
	<hr/>
	100.35 „
Oxygen equivalent to Cl,	0.65 „
	<hr/>
Total,	99.70 „

The average of two ultimate analyses of the fibre, freed from all impurities, showed that it differs from ordinary silk in its chemical composition, as will be seen from the following table:—

	Tussur Fibroïne.	Mulberry Silk Fibroïne.	
		Calculated for $\text{C}_{15}\text{H}_{23}\text{N}_5\text{O}_6$ (Mulder's Formula).	Calculated for $\text{C}_{17.4}\text{H}_{107}\text{N}_{5.4}\text{O}_{25}$ (Schützenberger's Formula).
	Per Cent.	Per Cent.	Per Cent.
Carbon,	47.18	47.78	50.26
Hydrogen, . . .	6.30	6.23	6.31
Nitrogen, . . .	16.85	18.90	19.84
Oxygen,	29.67	26.04	23.60
	<hr/>		
	100.00		

It contains, therefore, less carbon, about the same amount of hydrogen, considerably less nitrogen, and more oxygen than ordinary silk. This difference in the chemical composition is no doubt sufficient to account for the difference in the behaviour of the two fibres towards chemical reagents.

* *Journ. Soc. Dyers and Col.*, 1888, p. 88.

Behaviour towards Alkalies.—A considerable difference exists between the behaviour towards caustic soda of Tussur silk and ordinary silk; whereas the latter is soon dissolved in a boiling 10 per cent. solution of this reagent, Tussur silk requires a considerable time. A separation of the fibres may thus be effected. The same reaction may also be used for separating Tussur and wool in mixed fabrics or yarns.

Behaviour towards Acids.—Ordinary silk dissolves in concentrated hydrochloric acid (sp. gr. 1·16) almost instantly, while Tussur silk only partially dissolves if left for even 48 hours in the cold acid.

A similar difference is manifested in the behaviour of the two fibres towards concentrated *zinc chloride* solution, in which ordinary silk is readily and completely soluble, while Tussur silk is dissolved only after a considerable time, and then not completely. *Chromic acid* dissolves ordinary silk at once, while Tussur is only acted upon slowly.

Compared with ordinary silk, raw Tussur is, as a rule, a very impure article. Bastow and Appleyard found in a sample of reeled Tussur :—

Aqueous extract,	21·33 per cent.
Alcoholic „	0·91 „
Ethereal „	0·08 „

By boiling in distilled water and afterwards in soap solution, a total loss in weight of 26·49 per cent. was obtained. The ash of the raw product amounted to no less than 5·34 per cent. of the whole. Wardle* gives the following figures, but omits to state whether the Tussur silk examined was spun or reeled :—

Species of Silk.	Loss after washing in water at 46° C.	Loss after boiling in soap solution.
	Per Cent.	Per Cent.
China Tussur,	13·7	21
Indian Tussur,	9	11
China Silk,	2½	27
Japan Silk,	8	30
Italian Silk,	4	28
Bengal Silk,	6¾	30

Tussur silk possesses, even after successive treatments with alkalies and acids, a light yellowish-brown colour which is difficult to remove. It is more difficult to dye than ordinary silk, and this is accounted for, according to Wardle, by the different degree of solubility of the two silks. According to the same authority, the reason that the

* *Journ. Soc. Arts*, June, 1891.

dyeing of black on Tussur silk is difficult, arises from two causes, the first being the well-nigh impervious nature of the fibrillæ and their consequent impenetrability to the absorption of ordinary tinctorial and chemical agencies; and secondly, the flatness of the fibre, which causes the light to be reflected at different angles to that of the round fibre of ordinary silk. This difference of structure causes the natural brilliancy of Tussur silk to be seen in scintillations instead of evenly diffused over the surface, and the silk, however well dyed, has a speckled, shiny appearance.

Of other wild silks, the following may be mentioned:—

Eria silk, the product of the *Attacus ricini*, which is found in various parts of India. What silk is produced from this source is almost entirely consumed in the native industries. It resembles Tussur silk.

Muga silk is the product of the *Antheraea Assama*, and is a native of Assam. The fibre is either white or of a light brown colour, and is easier to dye than Tussur silk.

Yamamai silk, the product of the *Antheraea yamamai* is indigenous to Japan. In its microscopical appearance it is scarcely distinguishable from ordinary silk, except by the greater diameter of the fibre, which averages about 0.027 mm.

Sea silk or **Byssus** is the product of certain molluscs, principally *Pinna nobilis* and *Pinna rudis*, which inhabit the Mediterranean and which are collected principally on the shores of Sardinia and Corsica. The fibres, which are excreted by these molluscs for the purpose of attaching themselves to the rocks, are of a golden brown colour, very soft, elastic, durable, and glossy. The diameter of the fibre varies from 0.013 to 0.055 mm. It differs from ordinary silk in being insoluble in acids and alkalies.*

* Witt, *Chem. Techn. d. Gespinnstfasern*, p. 77.

PART III.

WATER.

THE quality of water used for washing, scouring, bleaching, and dyeing purposes is a matter of the greatest importance. The use of an unsuitable water in such operations has, in thousands of cases, resulted in faulty work. Goods are frequently damaged to a greater or less extent from no other cause, and yet, in many instances, because the water happens to be bright and clear, it is never or rarely suspected of causing the mischief. Just as many people imagine that well water, if bright and clear and sparkling, must of necessity be of good quality for drinking purposes. It is known, however, that water may possess all these qualities and yet be little better than filtered sewage. Absolutely pure water never occurs in nature; even ordinary distilled water is not free from traces of other substances. For practical purposes, however, distilled water may be taken as *pure* in considering the properties of water.

Pure water has the composition H_2O , and is a transparent, tasteless, inodorous liquid; colourless when seen in thin layers, but when a considerable depth is looked through, it appears of a pale greenish-blue to a deep blue tint. Under ordinary barometric pressure, water boils at the sea level at $100^{\circ}C$. and freezes at $0^{\circ}C$., the scale of the centigrade thermometer being constructed upon the melting point of ice and the boiling point of water. According to the thermometer which is commonly used in England (Fahrenheit's) the boiling point of water is 212° and the freezing point 32° . Since the boiling point of a liquid is dependent upon the pressure exerted upon its surface, the temperature of the water in a steam boiler is higher than $100^{\circ}C$. in proportion to the pressure of steam therein. With a pressure of 50 lbs. to the square inch, for example, the temperature of the water is $138^{\circ}C$. Water containing matter in solution boils under the ordinary pressure at a higher temperature than pure water. A saturated solution of common salt boils at $109^{\circ}C$., whilst a saturated solution of calcium chloride boils at $180^{\circ}C$. The amount of substances used in dyeing operations is, as a rule, too small to have any practical effect upon the boiling point of the solution. Where dye-vessels are heated by open

steam pipes, the liquid may appear to be in violent ebullition and still have a temperature of several degrees below 100°C . Water, when heated from 0° to 4°C . contracts in volume, thus forming a striking exception to the almost universal law that bodies expand on heating and contract on cooling. When heated above 4°C . water gradually expands in volume until it reaches 100°C . and passes off as steam. At 4°C ., therefore, water attains its maximum density. In other words, a given volume of water at 4°C . weighs more than at any other temperature. 10,000 volumes of water measured at 4°C . become rather more than 10,001 volumes at 0°C ., and about 10,440 at 100°C . When water freezes it undergoes a sudden expansion, equal to about one tenth of its volume. The force thus exerted is very great, the bursting of water pipes by frost being due to this cause.

AMOUNT OF SUBSTANCES DISSOLVED BY 1,000 PARTS OF
WATER (Grms. per Litre).

	Cold.	Boiling.
Potassium hydrate,	2,000	...
Sodium hydrate,	600	...
Calcium hydrate,	1.28	.79
Potassium chloride,	350	600
Sodium chloride,	360	404
Calcium chloride (anhy.),	2,000	...
Stannous chloride,	2,700	...
Potassium carbonate,	900	2,050
Sodium carbonate (anhy.),	160	490
Calcium carbonate,035	...
Potassium sulphate,	100	260
Sodium sulphate (anhy.),	150	425
Calcium sulphate,	2.3	2.1
Aluminium ammonium sulphate (common alum),	90	4,220
Ferrous sulphate (crys.),	36	320
Copper sulphate (crys.),	330	1,180
Potassium bichromate,	100	1,020
Sodium bichromate,	1,100	2,100
Potassium bitartrate,	4	105

Water is 815 times as heavy as air. One gallon weighs exactly 10 lbs. or 70,000 grains. The solvent properties of water are very great, greater in fact than those of any other liquid. The solubility of substances ranges from the merest trace to solutions containing much more solid matter than water. As a rule, the solubility of a substance increases with an increase of temperature. The exceptions,

comparatively speaking, are very few; calcium hydrate and sulphate being, perhaps, the most familiar examples. Some salts, alum for example, are exceedingly soluble in boiling water, and only slightly soluble in cold. Others again, such as common salt, although freely soluble, are but slightly affected by an increase of temperature. The table on the preceding page shows the solubility of some familiar substances in cold and boiling water.

Water also possesses the property of dissolving gases. The colder the water the greater the volume of gas dissolved. The following table shows the solubility by volume of some gases in water at the ordinary temperature, 15° C. :—

		Volumes of gas dissolved by 1000 volumes of water, (cc per litre).
Oxygen,	29
Hydrogen,	19
Nitrogen,	14.8
Carbon dioxide,	1,002
Sulphur dioxide,	43,504
Sulphuretted hydrogen,	3,233
Ammonia,	727,200
Hydrochloric acid,	462,000

On account of the remarkable solvent power of water all natural waters contain more or less solid and gaseous matter in solution, varying greatly in quantity and in kind according to the nature of the strata with which the water has been in contact. For technical purposes we may conveniently classify natural waters into (1) *Rain water*; (2) *Spring and well water*; (3) *River and surface water*.

Rain water collected under suitable conditions is the purest form of natural water, but as it falls through the air it takes up the various impurities present in the atmosphere. Rain is, so to speak, water naturally distilled from the earth's great reservoir—the sea. That which is collected in the country, is of course, purer than that of towns. Rain water invariably contains carbonic, nitric, and nitrous acids; ammonia, oxygen, and nitrogen, and, usually, traces of saline matter as well as finely divided organic matter. The rain water of large towns usually contains comparatively large quantities of sulphuric acid, derived from the combustion of sulphur in coal, in addition to small quantities of numerous other substances evolved from various manufacturing processes. After a long spell of dry mild weather the first shower of rain in such places is unusually rich in impurities. Rain water as actually collected, however, often contains many more impurities than those derived from the atmosphere, varying according to the nature of the roof upon which it has fallen. A slate roof gives the purest water. If collected upon lead or galvanized iron roofs small quantities of lead or zinc may usually be detected in the water. In many works, where only hard water is available, it would frequently be found advantageous

to pay some attention to collecting and storing rain water, especially for scouring operations. One inch of rain on an acre is equivalent to rather more than 100 tons or 22,400 gallons of water. With an annual rainfall of 35 inches an acre of surface will thus yield on an average about 2,500 gallons of good soft water per working day.

Spring and Well Water.—Of the water which falls upon the earth as rain, a portion evaporates, another portion runs off the surface forming brooks and rivers, and a third portion penetrates into the earth to a greater or less depth according to the nature of the strata. In some cases, after passing through a few yards of permeable strata, such as gravel, sand, or limestone, a less pervious stratum, such as clay, is reached where the water accumulates, and takes an underground course until the stratum crops out at the surface at a lower level. If a well be sunk along the course, the water obtained therefrom is known as a *shallow well water*. On account of the comparative ease with which such waters can usually become contaminated by sewage and drainage from cultivated land, farm buildings, &c., they do not, as a rule, form desirable drinking waters, although they may be very good waters for dyeing and other purposes. In some cases the permeable strata do not crop out at the surface, but dip down under others which are impervious or nearly so, when the water passes down to a great depth, and does not reappear at the surface unless it meets with a fissure and is forced upwards, forming a *spring*: or unless the overlying strata are bored through, so as to form an artificial spring or artesian well.

Spring and well waters usually contain considerable quantities of mineral matter derived from the rocks through which they have percolated. The salts most frequently found in such waters are carbonates, sulphates, chlorides, nitrates and silicates of calcium, magnesium, sodium, potassium, aluminium, and iron. Calcium and magnesium salts give to water the quality of "hardness," a term signifying the property which such waters possess of destroying the lathering properties of soap. Calcium and magnesium sulphates are soluble in pure water, but the carbonates (except in very small proportions) are only soluble in water containing carbonic acid. The rain, as it falls, contains a small quantity of carbonic acid; it acquires a further quantity from decaying vegetable matters in the soil, but a much greater amount from subterranean sources. When water is so highly charged with saline matter that it is unfit for either domestic or technical purposes it is commonly termed a mineral water, of which there are numerous kinds.

River water is principally composed of a mixture of rain, surface water, and spring water. It also frequently contains more or less drainage water from towns and villages, as well as numerous impurities from various works and factories. River water contains, as a rule, much less dissolved matter than spring and well water, due principally

to the admixture with surface water, which often contains very little matter in solution. A portion of the soluble matter in spring water is sometimes gradually deposited, owing to the disengagement of carbon dioxide. Carbonates of lime and magnesia and oxide of iron are thus frequently deposited in the beds of streams and rivers. Surface water from moorland districts is usually of a yellowish-brown or brown colour, due to the presence of peaty acids in solution and other forms of vegetable matter in suspension. River water usually contains a considerable quantity of suspended matter. The Thames contains from 15 to 30 grains per gallon; the Mississippi 56 grains, and the Ganges from 15 to 150 grains per gallon. In this way immense quantities of solid matter are carried into the sea. The Amazon contains only 2 grains of suspended matter per gallon, yet it discharges about 980,000,000 tons of mud into the sea every year.

For Technical purposes the matter in solution is of much more importance than that in suspension, since the latter may be removed with comparative facility by mere subsidence only or by filtration. The analysis of water is treated in another portion of this work (see under *Analysis*); but a few simple tests may be here given, which, if applied at the same time to a water whose composition and qualities are known, will frequently be found of service.

Calcium or lime salts are indicated by the formation of a fine white precipitate on the addition of a few drops of a solution of ammonium oxalate and ammonium chloride to the solution.

Magnesium Salts.—After adding ammonium oxalate in testing for lime, the liquid is boiled and filtered, and the clear filtrate evaporated to about one-tenth of its bulk. When nearly cold a little ammonia and sodium phosphate are added, which produce a crystalline precipitate in the presence of magnesia.

Sulphates, if present, will give a white precipitate on the addition of a few drops of hydrochloric acid and a little barium chloride.

Bicarbonates and free *carbonic acid* give a white precipitate on the addition of clear lime water.

Chlorides give a white curdy precipitate on the addition of nitric acid and silver nitrate.

Many natural waters when evaporated down to a small bulk become turbid. This may be due to the presence of either bicarbonates of lime and magnesia or sulphate of lime. If, on the addition of a few drops of hydrochloric acid, effervescence takes place, and the liquid becomes clear, carbonates only are present. If, on the other hand, no effervescence whatever occurs, and the liquid remains turbid, the deposit consists of calcium sulphate. The presence of both carbonates and sulphates is indicated by effervescence on the addition of hydrochloric acid, with but partial clearing of the liquid.

Waters containing salts of lime and magnesia give a white curdy precipitate when mixed with a solution of soap in weak alcohol,

and no froth or lather is produced until sufficient soap has been added to combine with the whole of the lime and magnesia present.

Iron, if present in considerable quantities, will usually form a reddish-brown deposit when the water is freely exposed to the air for some hours. Smaller quantities may be detected by evaporating nearly to dryness with addition of hydrochloric acid and a drop or two of nitric acid. If potassium ferrocyanide be now added, a blue precipitate or greenish-blue colouration will be produced, according to the amount of iron present. If potassium thiocyanate be added in place of ferrocyanide a red colouration will be obtained.

Alkaline carbonates may be detected by boiling the water for about ten minutes, filtering and adding either litmus, lackmoid, or phenol phthalein. The first two indicators are turned blue, the last red.

Acid waters turn a neutral solution of lackmoid red.

Organic matter in quantity gives to the water a brownish colour, and, in some cases, rises to the surface as a brown scum (especially if a little alum is added) when the water is boiled. Water containing organic matter when evaporated to dryness leaves a residue of a yellowish or brownish colour, which on ignition becomes at first darker brown or black. On continuing the heat, the separated carbon burns away, and the residue then becomes white or grey, unless much iron is present, when it is brown.

Water for Boiler Purposes.—In a steam boiler, since practically pure water comes off as steam, the solid matter in solution gradually accumulates and, in most cases, a portion of it, sooner or later, is deposited. If the deposit is of a loose, powdery character, it forms what is known as “boiler mud;” if it becomes firmly attached to the boiler plates it is known as a boiler “incrustation.” Waters which form a hard incrustation are either to be avoided for boiler purposes or they should be treated in such a manner as to prevent its formation. Incrustations not only cause much loss of heat, but the boiler plates are liable to be damaged through overheating. An incrustation is usually associated with a “hard” water, and there are many large users of steam who consider that incrustations are formed in proportion to the hardness of the water used. This is a mistake, since much depends upon the character of the salts constituting the hardness. A comparatively soft water may produce a hard scale much more quickly than a very hard one. If, for example, the hardness of a water was due entirely to either calcium chloride or magnesium sulphate (which is seldom the case, however), no incrustation would be formed under ordinary conditions, since both are very soluble salts. If the hardness of the water used is *entirely* due to bicarbonates, the excess of carbonic acid is quickly given off in the boiler and normal carbonates of lime and magnesia are precipitated, not on the boiler plates, but as a loose powdery mass. If the hardness is due entirely to sulphate of lime, no precipitation takes place until the water becomes very much concen-

trated—until it contains about 150* grains of calcium sulphate per gallon. At this stage, the water is saturated, and further concentration causes the calcium sulphate to crystallise on the boiler plates in the form of a hard deposit. When calcium and magnesium carbonates are present as well, these salts also become incorporated with the calcium sulphate. Water containing magnesium bicarbonate, deposits at first magnesium carbonate; but Driffeld, in a valuable paper on "Boiler Management"† has shown that boiler incrustations, though thrown down as a powdery mass, contain the magnesia in the form of hydrate, $Mg H_2 O_2$. He further points out that this hydrate of magnesia (even in the absence of calcium sulphate) is liable to bake into a hard scale if the flues are not well cooled down before the boiler is blown off. Calcium carbonate may also bake on to the plates under the same conditions, but not so readily as magnesium hydrate. In order to prevent the formation of scale in steam boilers, hundreds of so-called "boiler compositions" have been proposed and used. Some work satisfactorily, but the majority are altogether useless and, in some cases, positively injurious. A compound may, of course, act beneficially with one kind of water and yet be altogether useless for another. The best way is to remove the scale-forming ingredients, before the water enters the boiler, by one or other of the methods given under *Water Purification* (p. 67). Driffeld shows, however, in the paper above mentioned that very satisfactory results may be obtained by merely adding sufficient sodium carbonate to convert the calcium sulphate into calcium carbonate. Water containing magnesium chloride is liable to act injuriously upon the boiler plates, from its decomposition into magnesium hydrate with evolution of hydrochloric acid. If magnesium chloride, therefore, be present, sodium carbonate should also be added in sufficient quantity to convert it into carbonate.

Water for Scouring, Washing, and Bleaching Purposes.—

In all these operations salts of lime, magnesia, and iron are very objectionable. Iron is usually present in very much smaller quantities than lime and magnesia, but traces of iron in water are frequently the cause of much trouble. When soap is added to such waters no lather is at first produced, since the fatty acids of the soap combine with the lime and magnesia (as well as oxide of iron) to form sticky insoluble soaps possessing no detergent properties. No lather is produced until sufficient soap has been added to combine with the whole of the calcium and magnesium present. The soap is thus commonly said to be "killed." In this manner large quantities of soap are destroyed. One pound of calcium carbonate, or its equivalent in calcium sulphate or magnesium

* This figure represents the solubility of calcium sulphate under the ordinary atmospheric pressure. Under increased pressures, however, calcium sulphate is almost insoluble in water.

† *Journ. Soc. Chem. Industry*, vi., p. 178.

salts, dissolved in water, precipitates—and so far as its detergent qualities are concerned—destroys about 10 lbs. of good average soap. A water used for scouring yarn, recently submitted for analysis to one of the authors, was found to contain 35 grains of calcium and magnesium salts per gallon. Consequently, 1,000 gallons of this water (providing no free alkali were added as well) would destroy or render useless at least 50 lbs. of good soap. The “hardness” of a water is commonly expressed in degrees, but unfortunately some confusion exists regarding the exact meaning of the term. It may refer to parts of calcium carbonate (or equivalent in other salt) per 100,000; or to grains per gallon = parts per 70,000. Again, the hardness expressed in degrees may, or may not, include the hardness of pure distilled water. According to Wanklyn, distilled water has a hardness equal to 1 grain CaCO_3 per gallon. On Wanklyn’s scale a water containing 9 grains of calcium carbonate per gallon possesses a hardness of 10° , whereas on Clark’s scale (adopted by most chemists—or its equivalent in parts per 100,000) such a water would be 9° of hardness. Until comparatively recently, the hardness of a water was invariably determined by means of a standard solution of soap; but since other and more exact methods are now frequently employed (see under *Analysis*), it seems preferable to employ the term “degrees of hardness” as synonymous with either “parts CaCO_3 per 100,000,” or “grains CaCO_3 per gallon.” The latter form is employed in this work, unless otherwise stated. If the “soap test” were perfectly reliable and accurate, there might be some reason for allowing 1° for the pure water, but every chemist who has had any experience with waters knows that in many cases the “test” is most erratic. This has been clearly shown in a valuable paper on the “Examination of Water for Technical Purposes,” by A. H. Allen, in the *Journal of the Society of Chem. Industry*, 1888, p. 795.

A thousand gallons of water for every degree of hardness destroys about 1 lb. 7 ozs. of soap, but this loss of soap is not by any means the only disadvantage. The sticky, insoluble calcium and magnesium soaps which are precipitated are liable to be deposited irregularly on the goods, and such being the case, uneven dyeing—especially with “mordant” colours—is almost invariably the result. If more than a trace of iron is present in the water, an insoluble iron soap will be precipitated on the fibre, and on being subsequently dyed with any “mordant” colour, the shade will be dull and probably stained. For bleaching purposes, water containing iron is very objectionable, whether the goods are to be subsequently dyed or to remain white. Very small quantities of oxide of iron are sufficient to give a yellowish tinge to bleached fabrics, and to dull such shades as Turkey red. Water highly coloured with organic matter (peaty acids) is unsuitable for bleaching and stoving purposes.

Water obtained from the lower beds of the coal measures often

contains large quantities (20 to 40 grains per gallon) of sodium carbonate. Such water, in the absence of earthy carbonates, acts beneficially in scouring operations, and is highly valued by wool-combers and manufacturers who use large quantities of soap.

Water for Mordanting and Dyeing Purposes.—The most troublesome waters to the dyer are those containing iron (in any form), and carbonates of lime, magnesia, and soda. Sulphates have little or no action in dyeing, but in the subsequent washing operations a considerable amount of earthy sulphates in the water may act injuriously in certain cases by “saddening” or dulling the colours. In mordanting operations, the carbonates produce precipitates with salts of iron, aluminium, tin, &c., and reduce bichromates to neutral chromates. The active ingredient is thus rendered much less effective as a mordant. If organic acids or acid salts (such as tartar) are used, a portion is neutralised and thereby rendered useless. Alkaline carbonates act more powerfully in these respects than calcium and magnesium carbonates. In dyeing operations, carbonates modify the colours produced with various dyes—especially cochineal scarlets, which are rendered much bluer than shades dyed in pure water. Many colouring matters, such as methyl violet, victoria blue, coerulein, alizarin blue, &c., are precipitated by carbonates. The dye thus works on to the material in a loose form and in many cases produces stains. It is not thoroughly fixed; and, when rubbed, much of the colour is removed, and stains whatever material it comes in contact with. The injurious effect of carbonates in water is strikingly illustrated in the dyeing of alizarin blue and coerulein. In some cases, as, for example, in the dyeing of alizarin red (either upon wool or cotton), lime salts are decidedly beneficial when the material has been mordanted with aluminium compounds. The effect of acetate of lime in dyeing with alizarin upon wool has been clearly illustrated by Hummel.* Alkaline carbonates retard the dyeing of most colouring matters; a small quantity of sodium carbonate, for example, is sufficient to prevent logwood working at all. Earthy carbonates in moderate quantity produce deeper though duller shades with logwood, fustic, &c. In dyeing with “acid” colours, neither sulphates nor carbonates have practically any effect. The amount of acid used, as a rule, is great in proportion to the alkalinity of the water. And as large quantities of sodium sulphate are generally added at the same time, the comparatively small quantities of calcium, magnesium, and sodium sulphates (formed by the action of the sulphuric acid on the carbonates), cannot be expected to appreciably affect the results. In many cases, after the dyeing proper, the colour is seriously injured by washing or showering with water containing a large amount of earthy and alkaline carbonates. Too little importance is often given to the kind of water used in washing dyed goods. The effect of iron in water used for dyeing is to “sadden” or dull almost

* *Journ. Soc. Dyers and Col.*, 1884, p. 11.

all "mordant" colours. A very small quantity either in the mordant or dye-bath has a most marked effect upon shades produced with such colouring matters as alizarin red, cochineal, &c. The effect is much greater when separate baths are used for mordanting and dyeing than when the single bath method is adopted. In the latter case the bath is usually of an acid character, and the iron does not readily work on to the fabric. With "acid" dyes, the amount of iron usually present in natural waters produces little or no effect.

Lead is seldom present in water used for dyeing, but its action in wool dyeing has been studied by Rawson,* who finds that bright colours dyed in a neutral bath are very much affected, whereas in the presence of acids the same amount of lead has no action. The "saddening" effect is evidently caused by the sulphur naturally present in the wool combining with the lead to form black sulphide of lead. In the presence of sulphuric acid, however, this combination does not take place.

Correction of Water used in Dyeing.—Methods for the general purification of water are described below, but, in the absence of iron, for most dyeing purposes all that is necessary is to carefully neutralise the earthy and alkaline carbonates, which may be present, with an acid. This may be done in the mordant or dye-bath with either sulphuric acid or acetic acid. The former acid is much cheaper, but great care must be taken not to use too much; otherwise bad results will be obtained. On this account, in dyeing with alizarin blue, coerulein, and other similar colours in calcareous waters, it is much better to use *acetic* acid, since a slight excess does no harm. In mordanting with bichromates, sulphuric acid may be used with advantage for neutralising any carbonates. The amount of sulphuric acid (D.O.V.) required for 1,000 gallons of the water may be readily ascertained in the following manner:—Pour one litre of the water into a white basin and add a few drops of a solution of methyl orange. Add from a burette, during constant stirring with a glass rod, a solution containing $6\frac{1}{4}$ grms. of the same sulphuric acid in a litre of distilled water until the colour of the liquid changes to red. The number of cubic centimetres thus required corresponds to the number of ounces of sulphuric acid to be added to 1,000 gallons of the water.

PURIFICATION OF WATER.

The supply of water is frequently of such a quality that it is found desirable to effect some means of purification. On a small scale, for the laboratory, &c., water is best purified by distillation. In many works a considerable amount of distilled or condensed water is obtained from the steam pipes and used for scouring purposes. This practice might be much more widely adopted; the condensed water could not

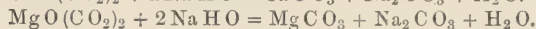
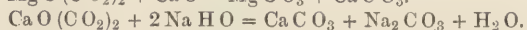
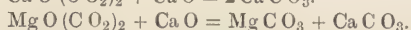
* *Journ. Soc. Dyers and Col.*, 1889, p. 58.

possibly be used to greater advantage. A pure soft water is a greater necessity in scouring than in any other operation.

Suspended matter in water is readily removed by filtration through beds of sand and gravel or engine ashes. Many other substances, especially iron, are wholly or partially removed by exposure to air in large shallow dams and subsequent filtration. Waters highly charged with bicarbonates give off a portion of their carbon dioxide, and normal carbonates are precipitated. Excepting waters containing ferrous carbonate, however, the change takes place very slowly and is never complete. Ferrous carbonate in water is quickly decomposed on exposure to air, and ferric hydrate is thrown down as a reddish-brown precipitate.

Several methods for the filtration of large quantities of water are described by A. Steiger in the *Journal of the Soc. of Dyers and Colourists* (1886, p. 185), as also in the *Journal of the Soc. of Chem. Industry* (1886, p. 416).

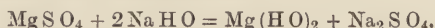
For the purification of water by chemical means numerous substances have been proposed. The principal impurities to be removed are bicarbonates and sulphates of lime and magnesia, as well as iron and organic matter. It has been already stated that bicarbonates in water are decomposed and precipitated by boiling. A similar effect is produced by adding calcium or sodium hydrate to the water. When lime is used, the free carbonic acid unites with it to form calcium carbonate, which is precipitated as well as the calcium or magnesium carbonate previously existing in the form of soluble bicarbonates. When caustic soda is used, sodium carbonate is formed, which remains in solution. The following equations illustrate the changes which occur:—



It is very important that the exact amount of precipitant should be added; otherwise, when lime is used, the water may be rendered harder than it previously was, either by a deficiency or an excess. If the water contains much free carbonic acid, a small amount of lime may be converted into bicarbonate and remain in solution. On the other hand, if too much lime is added, the whole of the carbonic acid is removed, but calcium hydrate remains in solution. The treatment with lime or soda also removes any iron which may be present in the water as well as a portion of the organic matter. When much organic matter is present, in order to obtain good results, it is necessary to employ some soluble salt of alumina or iron in addition to lime or soda. The alumina or ferric oxide formed carries down the organic matter, and also causes the carbonates of lime and magnesia to settle more rapidly. If the purified water is to be used for boiler or scour-

ing purposes, caustic soda should be used ; otherwise a salt of calcium will remain in solution, rendering the water hard.

Waters containing sulphates* of lime and magnesia undergo no change on boiling (unless highly concentrated), and are not acted upon by calcium hydrate.† Sodium hydrate acts differently according to whether sulphate of lime or sulphate of magnesia only is present, or whether carbonates are present as well. In the absence of carbonic acid, sodium hydrate produces no effect upon water containing calcium sulphate ; but magnesium sulphate is precipitated as hydrate, in accordance with the following equation :—



When carbonic acid is present in water, either free or as bicarbonate, on the addition of sodium hydrate, sodium carbonate is formed, which then reacts upon calcium sulphate with the formation of carbonate :—



Unless calcium sulphate is present in excess, the addition of caustic soda thus effects the removal of both carbonates and sulphates of the alkaline earths.

If the free carbonic acid present is but small in amount, or the calcium sulphate excessive, an addition of sodium carbonate must be made. Sodium carbonate also precipitates magnesium salts as carbonate ; but the hydrate of magnesia is less soluble than the carbonate, hence caustic soda is the best precipitant. The method of purification by means of lime is commonly attributed to the late Dr. Clark, of Aberdeen ; although, according to the late Dr. Angus Smith, the use of lime was first proposed about a century ago by Thomas Henry, of Manchester. In its simplest form, as originally devised, two tanks or reservoirs are employed, one being used for mixing the hard water with the requisite amount of milk of lime or preferably clear lime water ; and the other, to receive the purified water after the insoluble matter has been allowed to subside. A better plan is to have two mixing or precipitating vessels of such a size that each will hold sufficient water for a day's supply. The precipitated calcium and magnesium carbonates settle slowly, and the vessels used should, therefore, be shallow. On this account, a considerable space is required to carry out the process with success. Of late years, however, numerous machines have been devised with the object of economising space and time, as also of obtaining a continuous flow of pure soft water.

In the *Journal of the Society of Chemical Industry* (1884, p. 51), J. H. Porter describes an apparatus which is known as the **Porter-Clark** machine.

* Nitrates and chlorides are acted upon in a similar manner to sulphates.

† Calcium hydrate added to water containing magnesium sulphate produces a precipitate of magnesium hydrate, but a corresponding amount of calcium sulphate remains in solution.

Since that was published, Messrs. Porter & Sons have introduced several modifications. One form, representing a "New System of Reservoir and Tank Filtration," is shown in Fig. 15.

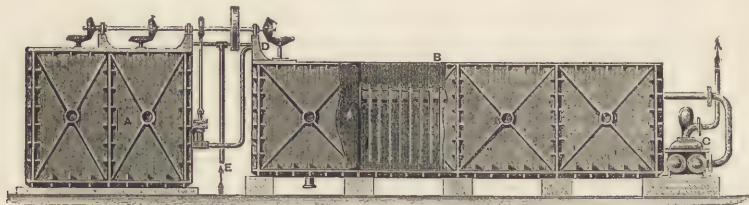


Fig. 15.—A new system of reservoir and tank filtration.

The tank, A, on the left is used for dissolving the lime or other reagents necessary to soften the water. The longer tank, B, consists of mixing chamber and filtering compartment. In the latter, the series of pendent filtering mats and cloths have their perforated pipes connected by a main pipe. When the softened water has to be raised to a higher level, the main pipe is connected with a pump, C, as shown in the figure. The filtering mats are made of cocoanut fibre, and covered with closely-woven twilled cotton cloth. Each set may be readily raised and cleaned without necessarily stopping the progress of the operation. The water is supplied to the two tanks by the pipe, E. It flows into the mixing chamber along with a regulated quantity of the necessary reagents at the point, D.

In a valuable paper entitled "Recent Improvements in the Treatment of Water for Technical Purposes,"* Macnab and Beckett

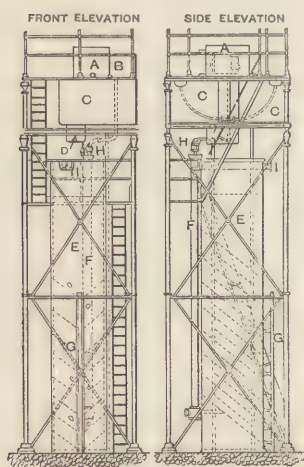


Fig. 16.

describe an apparatus invented by Messrs. Gaillet & Huet, which is known in England as the **Stanhope Purifier**. In the majority of cases treatment with a mixture of lime and caustic soda is found most suitable, although, of course, other reagents may be used when required. The following description is taken from the above named paper:—In the annexed diagram (Fig. 16) the same letters refer to the same parts in both figures. A is a store tank containing caustic soda solution of 46° Tw. (sp. gr. 1.231); B is a tank receiving the water to be treated, which is maintained at a constant level by means of a valve and float. C and C are two tanks for use alternately, in which the lime water is prepared, a measured quantity of caustic soda being

* *Journ. of the Soc. Chem. Industry*, 1885, p. 67.

added at each time of charging, this mixture constituting the reagent. D is a small tank for maintaining a constant head of reagent. E is the clarification tank in which the decantation is accomplished, and which will presently be referred to in detail. F is a large pipe in which the mixture of water and reagent takes place. G is a pipe in connection with cocks for drawing off the sludge as it accumulates in the angular spaces in the clarification tank. At H are the pipes provided with graduated quadrants for conveniently adjusting the quantities of water and reagents. I is the delivery pipe for the softened water. The clarification tank, E, contains a number of thin diaphragms or shelves of a V shape, inclined at an angle of 45° , as shown by the dotted lines; these are rivetted alternately to the two opposite sides of the tank, and their position forces the water to take a serpentine course through the tank. A bed of wood shavings, contained between wire nettings, in the positions indicated by the two lines of rivets near the top, serves as a safety filter to stop any particles which have escaped subsidence. The water supplied to the apparatus at B is conveyed by a pipe to H, where it flows into the mixing pipe along with the reagent from C and D, the quantities being regulated by the cocks at H. The mixture of the water and reagent being effected by falling together into the funnel of the pipe, F, precipitation at once commences, and the whole, travelling down the pipe, enters the clarification tank by a branch pipe near the bottom, whence it rises in a serpentine course to the top, whilst the clear and softened water overflows into the delivery pipe at I. The precipitate on settling out finds its way down the inclined shelves to the angular spaces connected with the sludge cocks, by opening which the mud is removed without interrupting the process. The whole operation is thus a continuous one, and the labour involved consists in discharging the precipitate by opening the sludge cocks about once a day, and in the preparation of the reagent at long intervals. In place of the two lime tanks, a simple automatic apparatus is sometimes employed for preparing the lime continuously.

Archbutt and Deeley have lately described, in the *Journal of the Soc. Chem. Industry* (1891, p. 511), a method of purification, which, at a comparatively small cost, has given excellent results. The process is carried out in plain tanks, but owing to the rapid method used of mixing the reagents with the water, and the subsequent treatment which the mixture receives, the precipitate is caused to settle very quickly and only comparatively small tanks are required. A special feature of the process consists in mixing the mud from the bottom of the tank obtained from previous operations with the water and the necessary reagents. This is found to have a remarkable effect in promoting the rapid subsidence of the precipitate.

The accompanying diagram (Fig. 17) shows the elevation and plan of a tank capable of softening 20,000 gallons at one operation. A¹ is

a piece of angle iron, fixed to one side of the tank, at a short distance from the bottom, below which the softened water is not pumped out ;

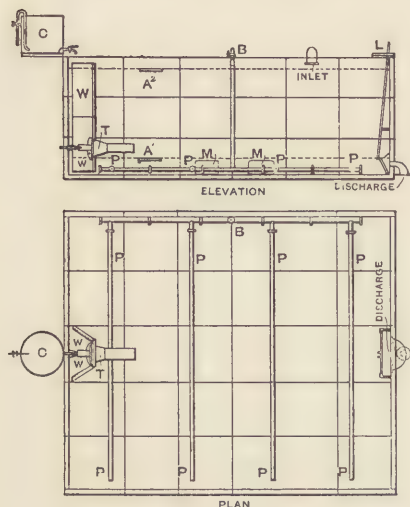


Fig. 17.

each operation is, therefore, commenced with the mud from previous softenings at the bottom of the tank and clear soft water above this as far as the lower angle iron. The tank is filled with the water to be purified as far as the upper angle iron, A^2 , and the necessary reagents boiled up with a few gallons of water in the small tank, C. The prepared liquid is then caused to flow into the well, W, fixed to the middle of one side of the large tank. This well is constructed of ordinary tank plates bolted together, and is freely open to the water in the large tank at the sides and at the bottom.

Near the bottom opposite a pipe which projects into the tank, there is fixed a steam injector, T, for the purpose of creating a powerful current of water from the well, through the projecting pipe into the tank. When this is put into action it causes the water and the reagents introduced into the well to become thoroughly mixed in about five minutes. A portion of the mud from the bottom is also stirred up and diffused through the water, but in order to more completely effect this purpose, perforated pipes, P, are laid along the bottom of the tank, a few feet apart ; and by admitting steam to the blower, B, air is sucked down the orifice and forced out of the perforations in the pipes. The result of this operation is, that the precipitate settles rapidly, and the water becomes so clear that in thirty minutes from the time of stopping the air current, it contains at a depth of 6 feet from the surface only about 1 grain of suspended matter per gallon. If the mud be not stirred up the precipitate takes at least 6 hours (usually more) to settle to the same extent. The water treated by Messrs. Archbutt & Deeley is that of the river Derwent after it has received the sewage of Derby. It contains both sulphates and carbonates of lime and magnesia with a considerable amount of organic matter, the total hardness being about 20° . The reagents used for this water consist of lime and sodium carbonate with crystallised aluminium sulphate in the proportion of about $1\frac{1}{2}$ oz. per 1,000 gallons. Ferrous sulphate may also be used in place of aluminium sulphate.

Water softened at the ordinary temperature (especially if magnesium

salts are present) after a period of about 24 hours (less if the temperature is higher) is liable to form a further small deposit of fine mud, consisting essentially of calcium carbonate and magnesium hydrate. This small deposit has little or no tendency to form a hard encrustation on boiler plates ; but it may produce mischievous effects in feed pipes, injectors, clack boxes, &c. Archbutt & Deeley have entirely overcome this difficulty by slightly carbonating the softened water. This is effected by impregnating the softened water in its passage to the storage tank with the gases given off from a coke stove.

Methods for the analysis of water are given in Part XI.

PART IV.

WASHING AND BLEACHING.

As they come into the market, the textile fibres are always in a more or less impure state, and the foreign substances adhering to them have sometimes to be removed before they can be manufactured, as is the case with wool; or they may be removed from the material in the manufactured state.

The object of washing and bleaching is to remove these impurities, as well as any substances which may have been used in the process of manufacture, either for the purpose of facilitating the spinning or the weaving—*e.g.*, oil for the spinning of woollen and worsted yarns, and animal or vegetable size for strengthening the warps in weaving.

The materials employed and the processes used for the cleansing or washing and bleaching of the different textile fibres vary considerably according to the nature of the fibre, and will consequently be described separately for each.

WASHING AND BLEACHING OF COTTON.

This may either be effected before spinning, or in the yarn or in the piece; the great majority of cotton goods are bleached in the piece.

Crude cotton contains, besides hygroscopic moisture, about 5 per cent. of impurities, most of which are insoluble in water but soluble in alkalis or acids. By boiling cotton in soda ash for $7\frac{1}{2}$ hours, and adding excess of dilute sulphuric acid to the resulting dark brown liquor, a copious, light brown, flocculent precipitate is obtained, while the liquid remains nearly colourless. This precipitate which contains the principal impurities in the cotton has been made the subject of a careful study by Dr. Schunck. When dried, it forms a brown, brittle, horn-like mass, translucent at the edges, and, when incinerated, leaves 2.3 to 6.9 per cent. of a light yellow non-alkaline ash. By suitable treatment Dr. Schunck was able to isolate from this residue the following substances:—

1. A wax-like body, which he called *cotton wax*, strongly resembling

the wax obtained from the leaves of the Carnauba palm. It is lighter than, and insoluble in, water; but soluble in alcohol and ether. It has a waxy lustre, is translucent, friable, and does not soften when kneaded between the finger and thumb. Treated with boiling dilute caustic soda, it melts without dissolving, and the filtered liquid gives only a trifling precipitate with acid.

The fact that raw cotton or materials made from it, are so difficult to wet out is probably due to the presence of a thin coating of this peculiar wax on the surface of the fibres.

2. A *fatty acid*, which melts at $55^{\circ}5$ C., and which appears to be either margaric or a mixture of stearic and palmitic acids.

3. Two nitrogenous, amorphous, brown *colouring matters*, one of which is easily soluble, the other sparingly soluble in alcohol. The darker shade of colour, seen in the so-called "nankin" cotton, is probably due to a great excess of these colouring matters existing in the fibre.

4. *Pectic acid*, which was obtained in the form of a light yellow amorphous substance resembling gum or gelatine. It dissolves in water to a clear and colourless solution, which reddens blue litmus. The substance is precipitated from its aqueous solution by acids and most metallic salts. Its compound with ammonia is precipitated from aqueous solution by neutral salts like sodium chloride or ammonium chloride.

5. Albuminous matter.

Of these various bodies, the pectic acid far exceeds the others in quantity; then follow the colouring matters. The three other constituents are present in extremely minute quantities only (*Schunck*).

Raw cotton yields 0.4 to 0.5 per cent. of ethereal extract.

RAW OR LOOSE COTTON.

Loose cotton is seldom bleached, since there is little demand for this article. The process employed is in principle identical with that used in yarn bleaching—viz., removal of the fatty and pectic impurities by boiling in alkaline liquids, and subsequently removing the colouring matters by means of chloride of lime. In the boiling with alkaline carbonates or caustic alkalies the fibres of loose cotton are apt to become matted under ordinary conditions. This difficulty could probably be obviated by some such machine as that of Jagenburg, which is specially constructed for the dyeing of loose cotton.* Or the boiling might be effected in a kier in which the cotton is divided into lots by means of a number of diaphragms.

Sansone† recommends the following process, which, he states, gives excellent results:—

1. The cotton is first worked until thoroughly impregnated, in a

* *Journ. Soc. Dyers and Col.*, 1887, p. 133.

† *Dyeing*, p. 45.

bath of sodium hypochlorite containing a small amount of carbonate, and standing at 2° to 4° Tw. until thoroughly impregnated, when it is allowed to steep for 3 to 4 hours or even overnight. It is then taken out, left to drain and washed.

2. It is then transferred to a bath containing bisulphite of soda at 2° to 3° Tw., worked for an hour and washed.

If the cotton is not perfectly white, the operations may be repeated.

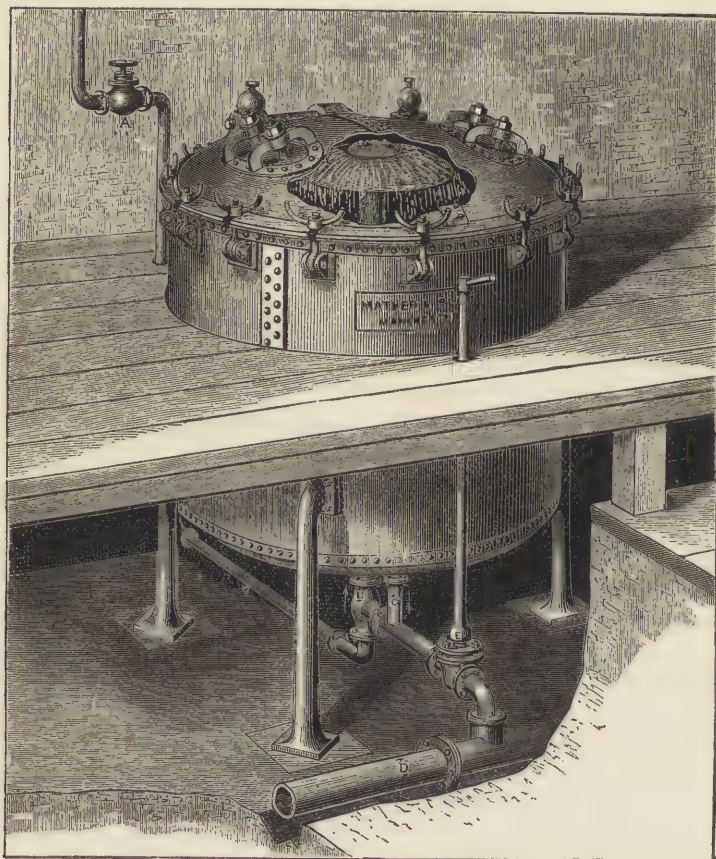


Fig. 18.—Low-pressure bleaching kier.

COTTON YARN.

When it is to be dyed subsequently in *dark colours*, cotton yarn is simply boiled in water or allowed to lie over night in soda ash for the purpose of removing the greasy impurities, which would otherwise render the even wetting out of the fibres difficult.

For the bleaching of cotton yarn, a more complicated process is necessary. The principal operations are:—*Boiling* in caustic soda or

soda ash ; *bleaching* in chloride of lime ; *souring* in hydrochloric or sulphuric acid ; and, lastly, for white yarn, *washing* and *blueing*.

The boiling with caustic soda is usually effected in open or low-pressure kiers, but in some works high-pressure kiers, similar in construction to those used for pieces, are preferred. On the other hand, low-pressure kiers are frequently used for pieces, especially in "market" bleaching. Fig. 18 shows the general appearance of a low-pressure kier, part of the lid being broken away in order to show the puffer pipe in the interior. It is constructed to work at a pressure of 5 lbs. When filled, the liquor (soda ash or caustic soda) is run in from above, the lid screwed down, and steam turned on at the valve. The steam passes through the injector, B, at the bottom of the kier, drawing with it the liquor which has collected underneath the false

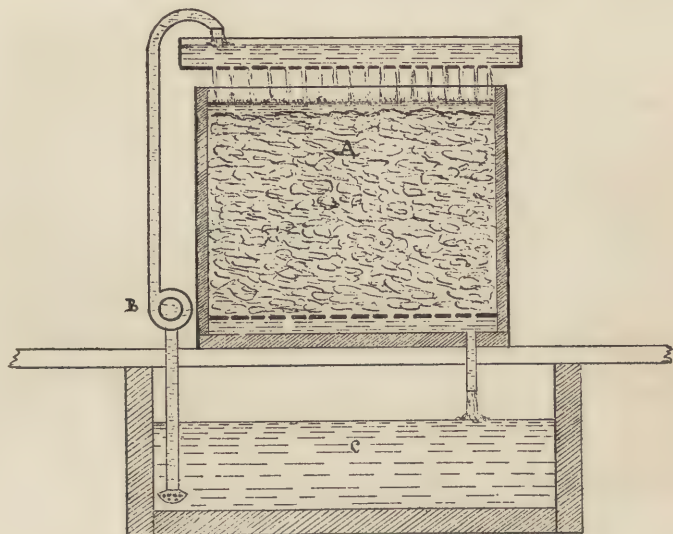


Fig. 19.—Cistern for yarn bleaching.

bottom. This is thus forced up the pipe in the centre, and showered over the goods, through which it percolates and collects again under the false bottom. D is the waste pipe through which the liquor is let off by the valve E, when the operation is finished.

The chemicking, souring, and washing off are usually done in a simple arrangement (Fig. 19), by means of which much hand labour is saved. This consists of a stone or wooden cistern, A, provided with a false bottom, into which the yarn is laid or packed evenly, so as to insure an even circulation. The liquor with which the yarn is to be treated is raised by means of a centrifugal pump from a well below the floor line in which it is stored, and caused to be thrown over the goods, through a perforated wooden tray. After percolating through the goods it accumulates below the false bottom, and flows back into the

well again. The strength of the liquor must, of course, be kept up by additions which are made from time to time.

The final washing of the yarn must be carefully effected in order to eliminate the last traces of acid which, if left in, would cause tendering. This is done either by hand or by machine, preferably the latter. A machine specially constructed for this purpose is that of C. G. Haubold, Jun. (Fig. 20). It consists of a circular iron tank containing a number (12 to 24) of square copper bobbins, which radiate from the centre, and on which the hanks of yarn are placed. All the bobbins move slowly in the same direction, and are caused at the same time to turn intermittently backwards and forwards round their own axis. By means of a partition placed in the tank, the water is caused to circulate in the opposite direction to that followed by the yarn, and

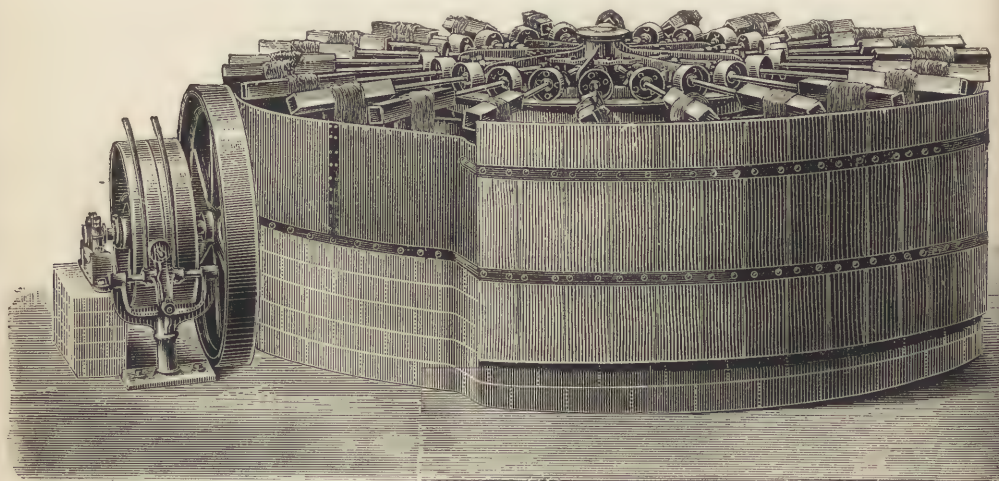


Fig. 20.—Haubold's yarn washing machine.

the washing is thus effected on the counter current system. Two men are sufficient to manage a large machine of this kind, one placing the hanks on the bobbins on that side of the partition on which the dirty water flows out; while the other standing next to him takes off the clean hanks on the other side of the partition, where the clean water flows in.

There are, besides, other washing machines which may be used for the same purpose. (See *silk washing*.)

In the improved arrangement of Mather & Platt (Fig. 21), the operations of boiling with alkali, chemicking, souring, and washing are all done in one and the same apparatus without moving the material, and thus a great deal of labour is saved, while the handling of the material is reduced to a minimum. The apparatus consists, as before, of a wooden cistern provided with a false bottom, into which the yarn is

evenly packed. The caustic soda lye is caused to circulate through a steam injector, being drawn from below the false bottom, and sprayed over the top of the cistern through a nozzle. After having been boiled for a sufficient length of time, the lye is let off, the goods are washed with water, after which there follows the treatment with bleaching-powder solution, which is drawn up from the well and showered over the goods by means of a centrifugal pump. The souring is effected in an analogous manner.

Washing and blueing are only necessary for yarn which is to remain white. The operation is usually carried out in wash stocks, as shown in Fig. 22. The yarn, A, is placed in a cavity, where, impregnated with soap and blue, it is subjected to the thumping action of the large

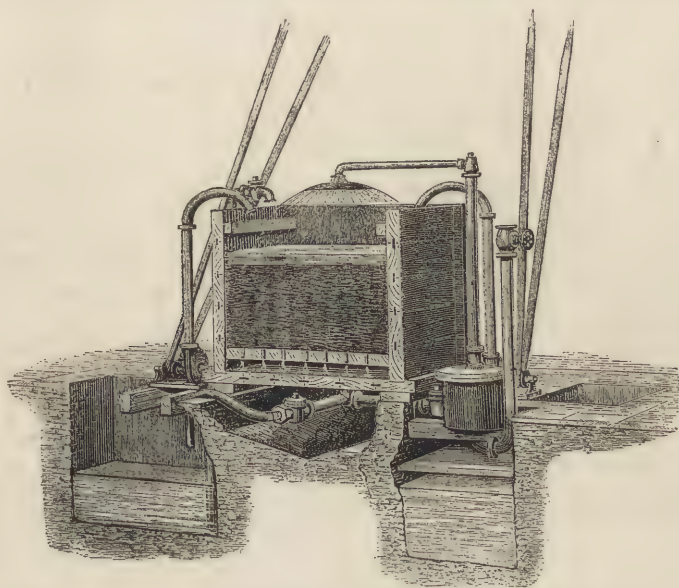


Fig. 21.—Mather & Platt's improved arrangement for yarn bleaching.

wooden hammer, B, which is caused to rise and fall by the revolving arms, C. According to another method, the washing and blueing are done continuously by tying the hanks loosely together, end to end, with short pieces of string, and passing them thus in rope form several times up and down through a bowl containing the soap solution and blue, and, lastly, between two heavy wooden rollers covered with cotton rope, the upper one of which lies with its axis in a slot, so as to press with its own weight only on the yarn, rising and falling as each hank passes through.

After washing and blueing, the goods are hydro-extracted and dried.

With respect to the details of the operations (strength of liquors,

duration of operations, &c.) observed in yarn bleaching, these will vary somewhat in all works. The following particulars may, however, be taken as typical :—

1. Boil 6 to 12 hours in low-pressure kier in soda ash (4 per cent. of weight of yarn).
2. Wash in open vessels ; 2 turns.
3. Chemick 2° Tw. 6 to 8 hours in circulating cistern.
4. Wash in cistern with water ; 10 minutes.
5. Sour in another cistern for 15 minutes with sulphuric acid at $\frac{1}{2}$ ° to 1° Tw.
If iron stains are present, use hydrochloric acid of the same density instead of sulphuric acid. Run off sour.
6. Wash in cistern ; 3 waters.
7. Soap, hydro-extract, and dry. With twofold yarns, use blue in the soaping.

The addition of a small quantity of soap in the ley boil greatly facilitates the removal of the wax-like constituents of the fibre.

The harder the twist of the yarn, the more difficult it is to bleach, and, consequently, with some yarns, it is necessary to repeat some of the operations in order to obtain a good white.

For small lots the following process gives good results :—
Boil 2 to 3 hours with 2 per cent. soap and 1 per cent. caustic soda ; wash, steep for 1 to 2 hours in chloride of lime at 2° Tw. ; wash and sour in

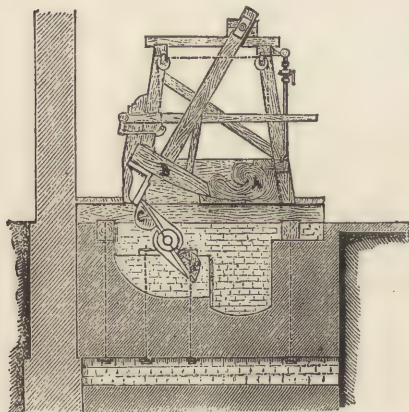


Fig. 22.—Wash stocks.

sulphuric acid at 2° Tw. ; steep one hour ; wash and soap.

BLEACHING IN THE COP.

Cotton yarn is sometimes bleached in the cop, as it comes from the spinning frames, in order to avoid the time and labour required for reeling it into hanks. To prevent it becoming entangled during the process of boiling, the cops are placed in baskets of wickerwork before being put into the kier.

COTTON PIECE GOODS.

The bleaching of cotton in the piece by far exceeds in importance that of bleaching in the yarn. Before the introduction of chlorine as a bleaching agent (first suggested by Berthelot in 1785, and carried into

practice shortly afterwards by James Watt), the operations of bleaching were simple but tedious; and consisted in boiling the goods in potash, steeping in buttermilk, and exposing them to the sun and air in fields. The introduction of sulphuric acid in place of buttermilk was said to be a great improvement, reducing the time required from 6 to 3 months. It was about the year 1837 when the present process, then known as the "American process," came into use; and it has, with slight modifications, remained in general use since that time. The following is a general outline of the process, as used for goods which are subsequently to be printed:—

1st Operation,	Singeing.
2nd	" Grey washing.
3rd	" Boiling with lime under pressure.
4th	" Treatment with weak acid.
5th	" Boiling with resin soap under pressure.
6th	" Boiling with soda ash under pressure.
7th	" Treatment with chloride of lime.
8th	" Treatment with weak acid.
9th	" Final washing and drying.

From this it will be seen at a glance that the bleaching of cotton pieces is a more complicated process than the bleaching of yarn. This arises from the fact that in cotton yarn we have simply the natural impurities of the cotton fibre to deal with, no additions being made during spinning. In cotton pieces, however, we have, in addition to these, the accidental impurities, such as grease from the machinery, finger marks, but principally the constituents of the size almost invariably employed for strengthening the warp before weaving. The size used for this purpose may contain a large variety of substances, such as farina, starch, soap, tallow, paraffin wax, &c. Small quantities of copper and lime soaps, compounds of iron and earthy matters may also be present in the material. Some of these impurities are removed by water alone, others by alkalies and soap, and the rest, with the exception of the natural colouring matter of the cotton, by acids. The removal of the natural yellow colouring matter of the cotton, or the bleaching proper, is effected by means of chloride of lime.

Marking and Stitching.—When brought to the works, the goods are deposited in the grey-room, where they undergo the preliminary operation of marking for the purpose of recognising the various lots afterwards and of tracing faults. They are then stitched together, end to end, by means of special sewing machines, and pass from the grey-room through guides or "pot-eyes" into the bleaching croft in continuous rope form, which shape they retain throughout the bleaching operations.

Singeing.—This operation is generally employed for those cotton

goods which are afterwards to be printed ; but it is also used extensively for other goods, such as unions, linings, corduroys, &c. The object of singeing is to remove, as far as possible, all the loose hairs from the surface of the cloth, and thus give it a clean face.

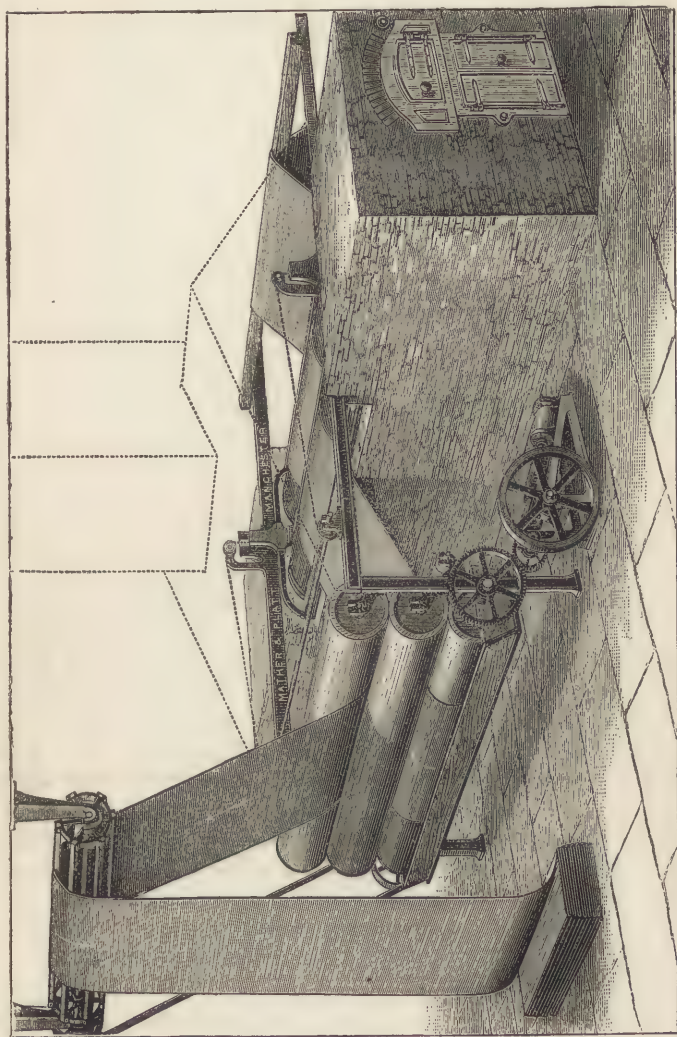


Fig. 23. — Plate-singeing stove.

Singeing is effected in three ways, viz. :—

1. Plate-singeing.
2. Singeing with revolving rollers.
3. Gas-singeing.

In plate-singeing the pieces previously stitched together, end to end,

in the grey-room are drawn at a rapid rate over two arched red-hot copper plates, and thence through a water trough to extinguish sparks.

The working of the system will be sufficiently clear from the figure. The rate at which the pieces pass over the plates is regulated by admitting more or less steam to the donkey-engine driving the rollers. Union goods are usually beamed off the singe-plates. A hood, indicated in the figure by dotted lines, serves to carry away the burnt products.

A drawback in plate-singeing is the unequal heating of the plates,

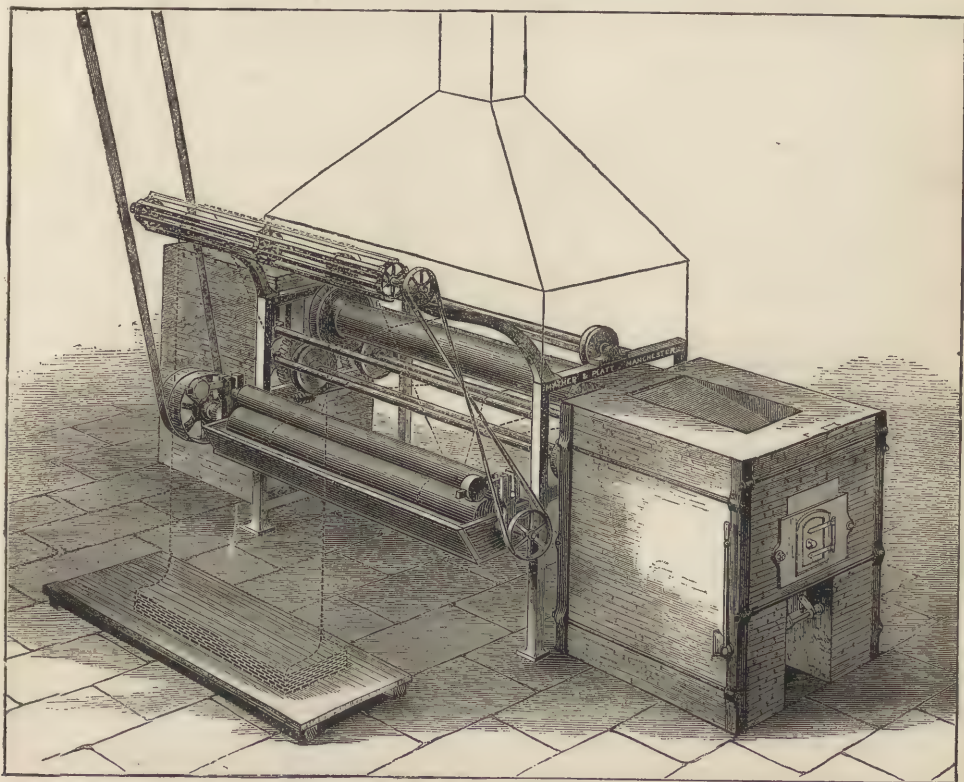


Fig. 24.—Singeing machine with hollow revolving roller.

which may give rise to uneven singeing. This difficulty is overcome by substituting for the plates a hollow cast-iron cylinder, which is caused to revolve slowly in a direction opposite to that followed by the pieces. The whole flame of the furnace passes through the roller into the flue on the other side, heating it to a uniform red heat. By such an arrangement the pieces come into contact with a continuously renewed surface of the roller and the singeing is more regular. Besides this, the pieces can be singed twice on the same side in one operation. The course of the pieces is shown in the figure by dotted lines.

Singeing by means of gas is more convenient than either of the foregoing methods, and is necessary for figured goods, corduroys, &c., on account of the unevenness of the surface. Formerly the flame was drawn right through the material, but, although otherwise effective, this method was soon abandoned, since it was found to impoverish the fabrics too much. In the present systems of gas-singeing, the pieces are passed over rollers of small diameter while being exposed to the action of a Bunsen gas flame, thus causing the "nap" to stand out as much as possible.

Figs. 25 and 26 show two different arrangements for singeing by gas. In the first, the pieces, after having passed over the rails, R, pass over

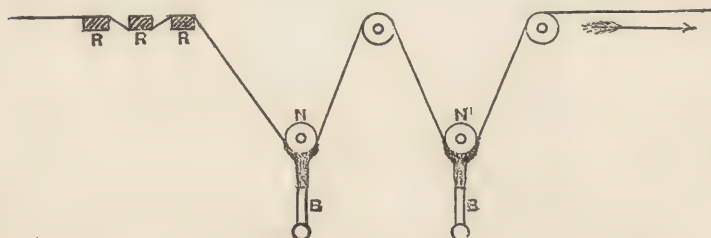


Fig. 25.—Gas-singeing.

the nap roller, N, directly underneath which there is a row of Bunsen burners. Thence they pass over the second nap roller, N¹, to another

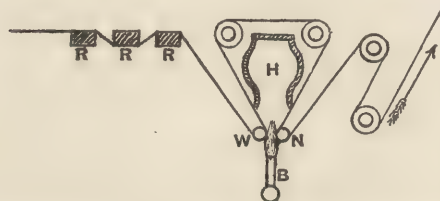


Fig. 26.—Gas-singeing.

row of Bunsen burners, which are so placed as to singe those parts left in between the burners of the first row.

In the second arrangement a similar principle is adopted, but the material is brought twice into contact with the same flame. The

burnt products are drawn off by the hood, H, which runs across the whole breadth of the machine.

In the more recent gas-singeing machines, the gas, previously mixed with the necessary quantity of air for its combustion, is supplied to the burners under pressure from a Root's blower. By this method a higher temperature is produced in the flame, and a considerable saving in gas is said to be thus effected.

Cotton, worsted, and spun silk *yarns* are frequently singed or "gassed" for the purpose of producing a clean yarn—*i.e.*, a yarn free from loose fibre on the surface—by passing them at a rapid rate through gas flames. The singeing of worsted yarns is known as "genapping."

Grey Washing.—This operation is sometimes omitted, not being

absolutely necessary. It consists in passing the goods coming from the singe house through water in an ordinary washing machine and then allowing them to lie in a heap over-night. The result is that part of the matters soluble in water is removed; the material becomes thoroughly wetted, and the starchy matters become soluble in con-

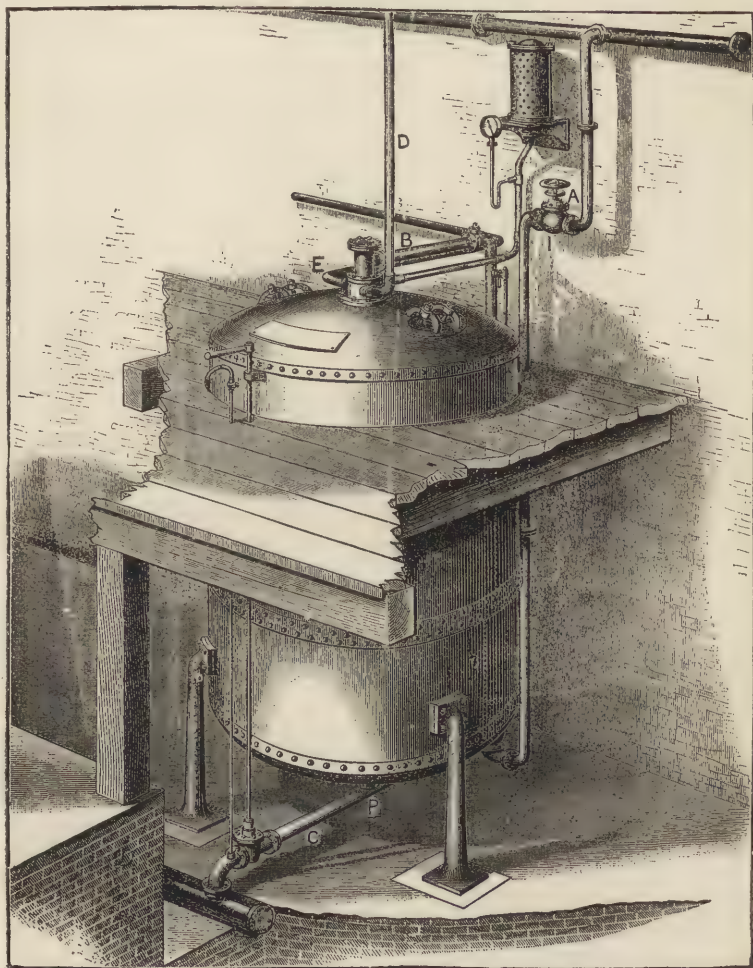


Fig. 27.—Injector-kier (Mather & Platt).

sequence of a fermentation, which sets in and which frequently manifests itself through a considerable rise in temperature in the goods.

Lime Boil.—In this operation the goods are subjected in kiers (large cylindrical vessels of wrought iron) to the action of lime water, generally at a high temperature and under pressure. In all the various systems of kiers, the lime water is caused to circulate con-

tinuously through the goods during the operation, and this is effected in various ways.

The kier in most common use among bleachers is the injector-kier (see Figs. 27 and 28); so-called because the circulation of the liquid is effected by means of a steam injector. The steam, which is turned on at the valve, A, passes down to the bottom of the kier and through the

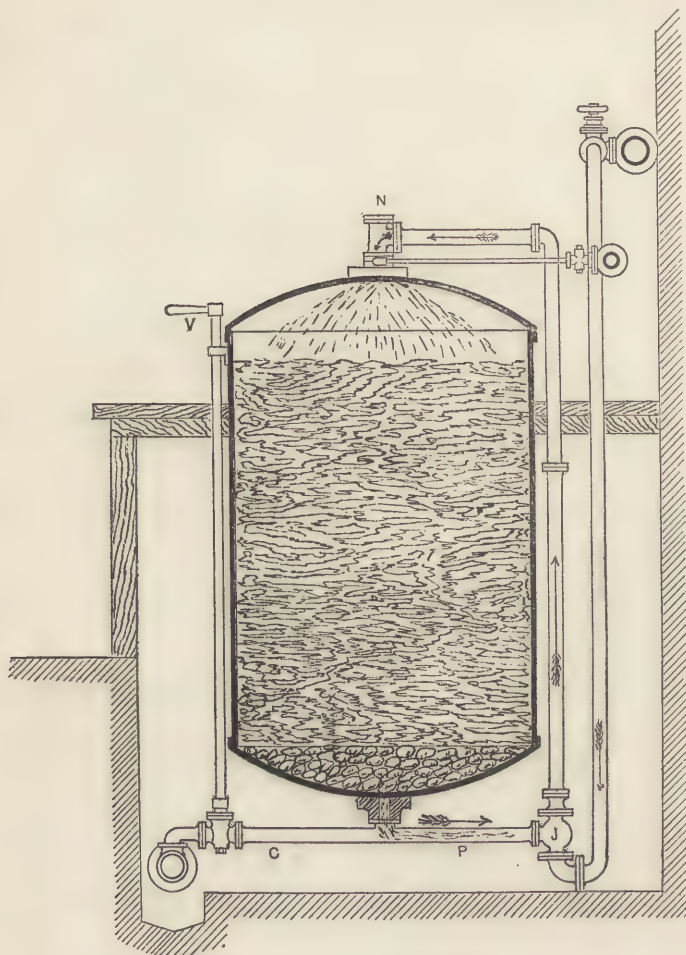


Fig. 28.—Section of injector-kier.

injector, J (shown in the dotted lines behind the kier), drawing the liquid through the pipe, P, from beneath the false bottom, and forcing it up to the top through the pipe, B, which conveys it through the nozzle, N, back into the kier again. Water is supplied through the pipe, E; liquor from the pipe, D, while C is the waste-pipe, which can be opened or closed from the working floor by the handle, V.

Kiers are constructed for quantities of cloth varying from 600 to 3,500 lbs., the diameter ranging from 1·3 to 2·1 metres, and the height from 1·8 to 3 metres.

In working, the calico to be bleached is first passed through milk of lime, which is made of such a consistency that the material takes up about 5 per cent. of its weight of lime; or an amount of milk of lime corresponding to 400 grms. of burnt lime to each 100 metres of calico. The milk of lime should be passed through a sieve before use, in order to remove small stones, &c. It is then packed evenly into the

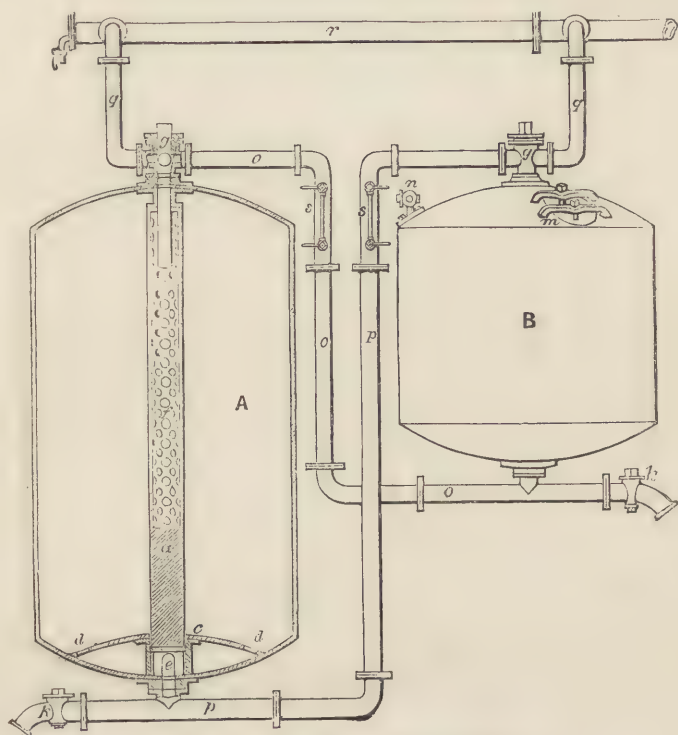


Fig. 29.—Pendlebury high-pressure kiers.

kier by boys, who fold it with short sticks, and then press it down by treading on it. The necessary amount of water is then run in; and, after the air has been got rid of by blowing in steam for a short time, the kier is closed, and the boiling is continued under pressure.*

Two other systems, which are also in use, viz., those of Pendlebury and Barlow, may also be mentioned here.

In the Pendlebury system two kiers are employed—a larger one, A, which contains the goods, and a small one, B, which contains the ley.

* The pressure employed varies in different works from 10 to 70 lbs., the time necessary being inversely proportional to the pressure.

After the air has been driven out of the larger kier by blowing in steam for about half an hour, the draw-off tap, *k*, is closed, and the boiling alkaline ley is forced over from the smaller kier. The large kier is then heated for some time by direct steam, when the ley is forced back into the smaller kier. This alternating process goes on for about four hours, when the operation is finished.

In the Barlow system two kiers are also employed; but it differs from the Pendlebury system, inasmuch as both kiers are of the same size and are each filled with goods.

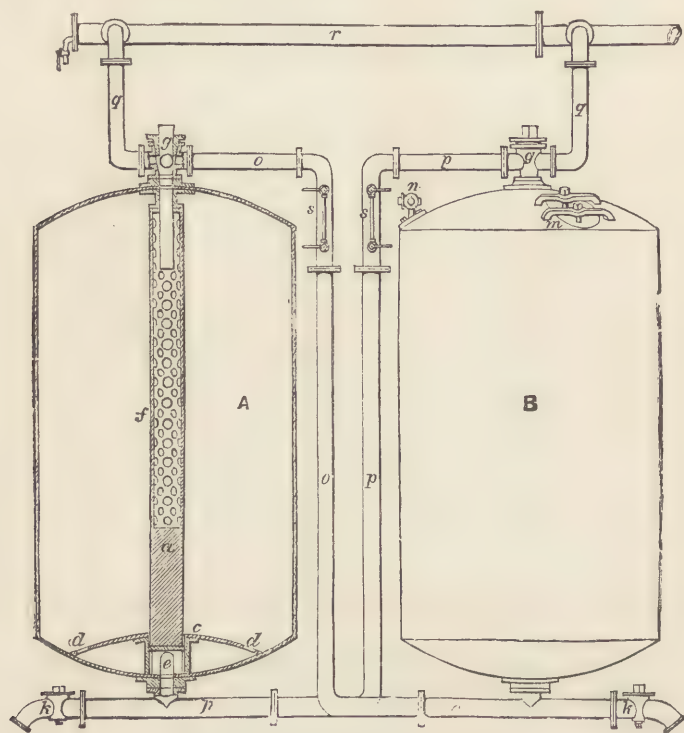
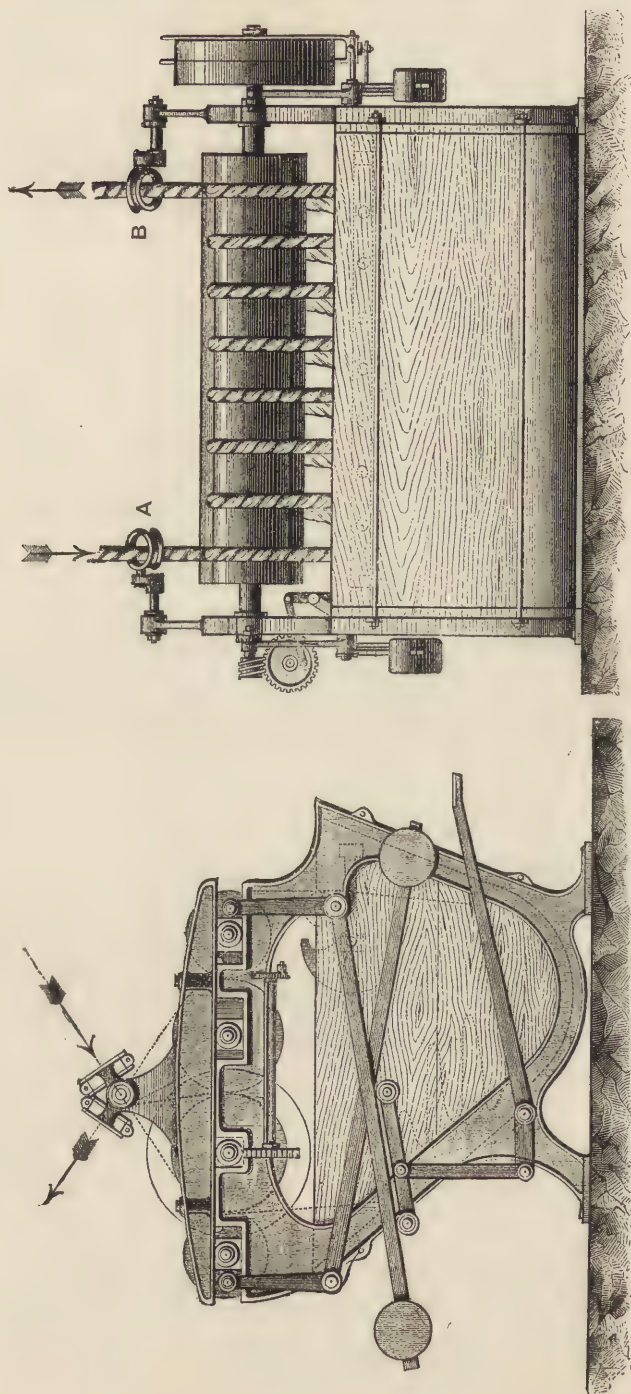


Fig. 30.—Barlow's high-pressure kiers.

After both kiers have been filled with pieces, the manholes, *m*, are closed, the draw-off taps opened, and steam is blown through in order to displace the air and moisten the material. The draw-off taps, *k*, are then closed, one of the manholes opened, and the necessary amount of liquid admitted. The manhole is then closed again, and high-pressure steam is admitted to both kiers. After the liquid has boiled for a time in the first kier, it is forced over into the second by simply changing the position of the two-way cocks, *g*. While the goods in the second kier are being boiled in the liquor, those in the first are being acted upon by high-pressure steam. After a time the cocks are



Figs. 31 and 31a.—Haubold's machine for liming, chemicking, and souring.

again reversed, and this alternating process is continued for 4 to 6 hours.

Formerly Barlow's kiers were much in demand; but, from private information received from one of the largest makers, about 70 per cent. of those delivered have been converted into injector kiers at the request of the users.

The Pendlebury-Barlow high-pressure kier is a combination of the two systems just referred to, having two large kiers for holding the goods and one small one in the middle in which the ley is heated.

The lime kiers are whitewashed from time to time on the inside in order to prevent the material getting rust stains by coming into direct contact with the iron.

After the lime boil, the liquor is allowed to run off, so that it is necessary to fill the kier as rapidly as possible with cold water before taking the pieces out. If this is omitted, the lime dries on the fabric where the latter touches the hot walls of the kier, and becomes so concentrated in those places that it is but incompletely removed in the subsequent souring. After printing and steaming, brown stripes are found here and there across the piece, and in these places the fabric is found to be tendered.

The impregnating of the pieces with milk of lime previous to their entering the kiers may be effected by means of the machine shown in Figs. 31 and 31a. The same, or a similar machine serves for chemicking and souring. The pieces pass in through the guide, A, and leave again at B, after having been passed several times through the milk of lime in the vat in order to ensure even impregnation. The machine is provided with four wooden rollers, to one of which a pulley is attached, and this serves for driving the others, the bearings of which lie in slots. The pressure, which is lateral, is produced by the levers and weights shown in the side elevation. In order to avoid wearing grooves into the rollers, the guide pegs are provided with a to and fro motion by means of a wheel and ratchet, so that the strands in passing through do not always come in contact with the same parts of the roller. By an automatic arrangement, the machine is thrown out of gear if a knot should form in one of the strands and get between the rollers.

The chief effect of the lime boil is to decompose the fatty and oily matters contained in the pieces. The fatty lime soaps which are thus formed adhere to the fibre, but are completely removed in the subsequent processes. In addition to this, starchy and other soluble matters are removed, and the natural impurities are so chemically changed as to be more easily eliminated in the subsequent processes. The colour of the material is actually darker after the lime boil than in the grey. This is especially noticeable in goods made from Egyptian cotton.

On coming from the kier the goods are washed in washing machines for the purpose of removing the soluble impurities and as much of the lime as possible before passing on to the next operation.

The washing is effected in a machine like that shown in Fig. 32, which is constructed to take two strands at once. The pieces pass in at each side through the pot-eyes, between the wooden bowls, round the roller at the bottom of the trough and up again through the bowls, and so on, being guided in their course through the machine by the

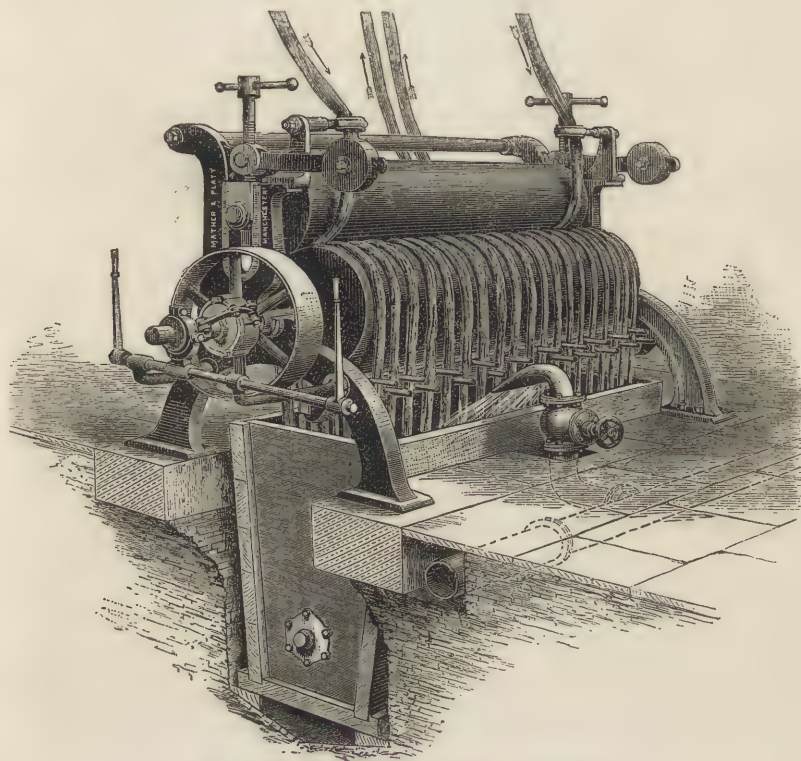


Fig. 32.—Mather & Platt washing machine.

wooden pegs shown in the figure. Both strands leave the machine at the centre on the side opposite to that on which they enter.

The following treatment with weak acid is known as the *grey sour* or *first sour*, and consists in running the goods through sulphuric or hydrochloric acid at 1° to 2° Tw. in a machine identical in construction with that shown in Fig. 31. The souring is effected in the cold, but recently better results are said to have been obtained by souring at a temperature of about 80° C. with a much weaker acid ($\frac{1}{2}$ to 1 grm. per litre).

The effect of the grey sour is to decompose the lime and other

insoluble soaps on the fibre and to remove metallic oxides (iron stains, &c.). The free fatty acids which result from the decomposition of the insoluble soaps remain on the fibre, but are readily removed in the next operation.

After the grey sour it is necessary to wash well, in order to remove, as completely as possible, the acid retained by the pieces. If this is omitted a tendering may take place in the next operation.

The First and Second Ley-boils.—The goods are now boiled twice with soda, generally in high-pressure kiers of the injector type (see above).

In the first ley-boil they are treated with 5 to 6 per cent. of their weight of soda ash and $1\frac{1}{2}$ to 2 per cent. of resin previously dissolved by prolonged boiling in the necessary amount of caustic or soda ash. Working under a pressure of 3 to $3\frac{1}{4}$ atmospheres, the operation lasts from 3 to 4 hours, while for low-pressure kiers 12 hours are requisite.

The second ley-boil is carried out like the first, but soda ash alone is used (1 to 2 per cent. of the weight of the material).

The effect of the ley-boils is to dissolve the free fatty acids left on the fibre after the grey sour. The effect of resin soap, which is only used for goods which have subsequently to be printed, is to remove certain constituents of the fibre which evince a slight affinity for colouring matters, and which, if left in the fibre, would leave the whites dull in printed goods.

In some works, the goods are boiled with soda alone previous to the treatment with resin soap. Although not indispensable, Hummel considers this operation advantageous, since the last traces of acid left in after the washing following the grey sour are entirely neutralised, and the danger of tendering in the subsequent ley-boil with resin soap is thus averted. The addition of a small quantity of heavy mineral oil in the ley-boil is said to economise bleaching-powder in the subsequent operation of chemicking.

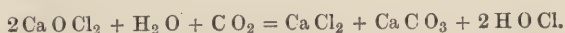
After the ley-boils, the goods are again washed in the washing machine. At this stage the cotton has been freed from all the impurities soluble in water, acids, alkalies, and soap-emulsion.

Bleaching.—This process, also known as *chemicking*, has for its object the destruction of what remains of the natural colouring matters in the fibre. It is effected by passing the goods through a clear solution of chloride of lime or bleaching-powder, standing at $\frac{1}{2}^{\circ}$ to 2° Tw. in a machine similar in construction to that shown in Fig. 31. For dissolving the chloride of lime an apparatus may be used like that shown in Fig. 33.

It consists of a square cast-iron lead-lined vessel, containing a wrought-iron perforated drum, which is also lead-lined. The bleaching-powder and the water are put in through the lid shown at the top of the drum, which is caused to revolve by means of a pulley on the outside. The solution is drawn off by means of a tap, which is placed

at a sufficient distance from the bottom to avoid drawing off the sediment. For the removal of the latter a valve is provided.

After leaving the machine the goods are piled in a heap, and left exposed to the air for some time, before undergoing the next operation. This gives the chloride of lime time to act on the colouring matter, and it is assisted to a considerable extent during the exposure of the goods by the carbonic acid of the air, which liberates from it free hypochlorous acid :—



The *white sour*, which now follows, effects the complete decomposition of the chloride of lime still remaining in the fibre, and the removal of the lime from the fibre, providing that the goods have not been washed after chemicking. Generally, however, the goods are washed after chemicking, and the sour then simply effects the removal of the lime. For the white sour, either hydrochloric or

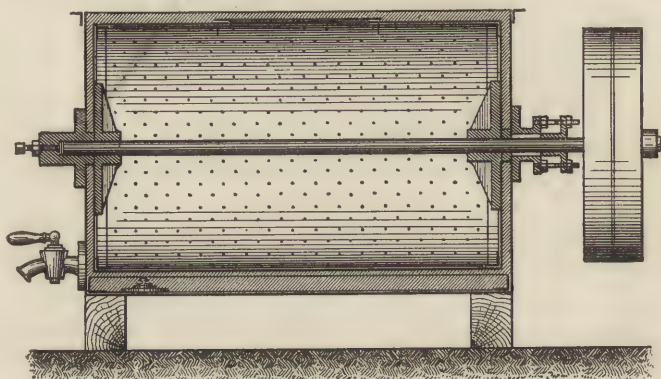


Fig. 33.—Haubold's apparatus for dissolving bleaching-powder.

sulphuric acid, at 1° to 2° Tw., are used, and the operation is carried out in the same machine as the grey sour.

The bleaching proper is now finished, and the only operations which follow are the *final washing* in washing machines, the opening out and drying over copper cylinders. It is necessary that the final washing should be carefully carried out, in order to remove the last traces of acid, which, if left in, would render the fabrics liable to become tendered in the drying. For the final washing, the square beater washing machine (Fig. 97) renders good service.

The final washing and squeezing, for the purpose of removing as much water as possible before drying, may be effected in a machine like that shown in Fig. 34, in which the pieces first pass through a water trough, thence through the squeezing rollers, down to the bottom of the second trough, through the squeezers again, and out. In market bleaching, the first trough serves for blueing.

The following two bleaching processes are cited by Lauber (*Handb. d. Zeugdrucks*) from practice. The first is that of John Barlow, which was in use in 1872-73 :—

1. Wet out in grey washing machine ; allow to lie for 24 hours and wash.
2. Pass through milk of lime (400 grms. Ca O for every 100 metres of calico), with little pressure on the squeezers, so that the pieces can take up as much lime as possible. It is preferable to take too much

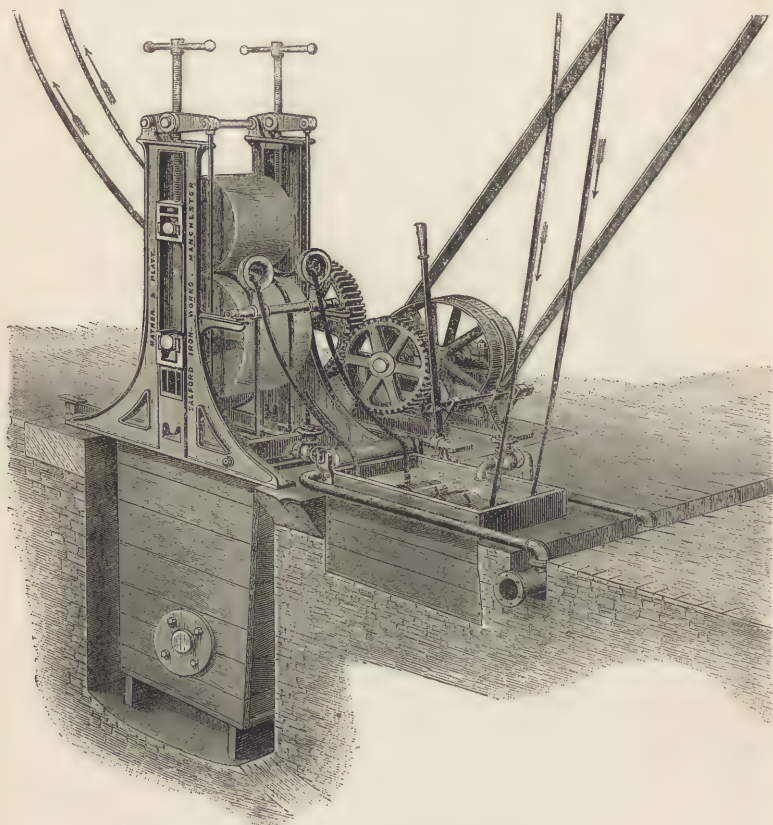


Fig. 34.—Squeezing rollers for calico.

lime than too little lime ; according to Lauber, a properly carried-out lime boil is the foundation of a good bleach ; if it fails, the fault cannot be made good, even by using twice the usual quantity of soda and resin in the subsequent ley-boil.

3. Boil for 6 hours.
4. Wash twice. After the second washing squeeze well, in order to prevent the dilution of the subsequent bath.
5. Sour in sulphuric acid at 3° to $4\frac{1}{2}^{\circ}$ Tw. Allow to lie 3 to 4 hours.

6. Wash twice. From the second washing machine the pieces are led straight into the kier.

7. Boil 6 hours in resin soap.

8. Wash twice. Squeeze well after the second washing.

9. Pass through chloride of lime at $\frac{1}{3}^{\circ}$ to $\frac{1}{2}^{\circ}$ Tw. Allow to lie in heaps of 20 pieces each until a good white has developed.

10. Wash.

11. Pass through sulphuric acid at 3° Tw. Allow to lie for 1 hour.

12. Wash twice and dry.

The following is another but a more recent process:—

1. Boil with lime for eight hours in high-pressure kiers at 2 atmospheres pressure.

2. Wash twice.

3. Sour with sulphuric acid at $4\frac{1}{2}^{\circ}$ Tw.

4. Wash.

5. Boil for 10 hours with soda (110 kilos. for 3000 metres calico) at 2 atmospheres pressure.

6. Wash.

7. Chemick with chloride of lime at $\frac{1}{3}^{\circ}$ to $\frac{2}{3}^{\circ}$ Tw.

8. Wash.

9. Sour with sulphuric acid at 3° Tw.

10. Wash three times and dry.

Another process, in use in the works of Messrs. Koechlin, Baumgartner, & Co., of Loerrach, with Barlow's high-pressure kiers, before the introduction of the Mather kier, is as follows:—

1. *Lime Boil*.—Pass through milk of lime (250 grms. lime for each piece) and boil under high pressure for 12 to 24 hours, according to the size of kier employed. For one holding 500 pieces, 24 hours are required, but a better result is obtained in 12 hours in a kier holding 250 pieces. Wash.

2. *Sour*.—Hydrochloric acid at 3° Tw. Allow to lie in acid for from 6 to 8 hours. Wash twice in washing machine.

3. *First Ley-boil*.—Boil together for 10 hours 80 kilos. soda ash and 30 kilos. resin. The pieces are boiled 6 hours under 60 lbs. pressure with this lye, and washed.

4. *Second Ley-boil*.—Boil together for 10 hours 160 kilos. soda ash and 60 kilos. resin. Boil the pieces in the kier with this lye 12 to 14 hours under 60 lbs. pressure.

Wash well in kier, then in washing machine.

5. *Chemick*.—Chloride of lime at $\frac{1}{3}^{\circ}$ Tw. Allow to lie 6 to 8 hours. Wash.

6. *Sour*.—Pass through sulphuric acid at $1\frac{1}{2}^{\circ}$ Tw. Wash twice in washing machine and dry.

The mean duration of the bleaching process for goods to be printed (madder bleach) is about five days.

Market Bleaching.—For goods which come into the market in the

white state, the bleaching process differs slightly from that described for printed goods. The singeing is generally omitted, the lime boil is frequently done in low-pressure kiers, and soda ash is substituted for the resin soap in the first ley-boil. In some bleach works, the chemicking is done between the two ley-boils. After bleaching, the goods are blued, either before or in the finishing. In market bleaching, the chemicking and souring are sometimes done in cisterns, as in yarn bleaching. The liquors are used over again, and a saving in material, amounting from 20 to 30 per cent., is thus said to be effected. The finishing operations are of great importance in market bleaching, and include starching, filling, damping, beetling, calendering, chasing, &c., by which both the appearance and the feel of the material may be considerably altered.

Bleaching for Turkey Red.—For goods which are subsequently to be dyed Turkey red, a full bleach is not necessary; in fact it is actually injurious, the treatment with chloride of lime preventing the production of a full bright red. This is due, according to Lukianoff,* to the presence of oxycellulose in the bleached cotton, which prevents, to a certain extent, the proper fixation of the mordants. The process generally adopted consists in giving the goods, after boiling with water alone, either one or two ley boils with caustic soda, after which they are soured with sulphuric acid, well washed and dried.

The theory of the ordinary bleaching process has already been touched upon in describing the various operations. The most important modern researches on the subject are those of M. Albert Scheurer, published in the *Bulletin de la Société industrielle de Mulhouse*. The following interesting account of his experiments is taken from an abstract of the original paper, which appeared in the *Journal of the Society of Dyers and Colourists*, in 1889:—

“*The Two Stages in the Bleaching Process.*—These are the removal by saponification of the fatty matter from the material, and the destruction of the natural colour of the unbleached cotton. To obtain a uniform white, the saponification should precede the decolourisation.

“The fatty matters which are present in the material, natural to cotton or acquired accidentally, protect the colouring matter from the action of the bleaching agents.

“Thus, where a stain of incompletely saponified oil remains, the fabric retains its natural colour; whilst when the oil has been removed by the ley-boil, the fabric is bleached.†

“A stain of this kind is removed only by the prolongation of the ley-boil; but when only a single ley-boil is used, the white on the part sensibly differs from the whole. It is therefore of the first importance to saponify the fatty bodies as

* *Journ. Soc. Dyers and Col.*, 1886, p. 29.

† Not only have alkalies more effect on the colouring matter after all the oil has been removed, but also the sun's rays. If a sample, which has been lime boiled, soured, and boiled one hour, be exposed to the sun, along with a sample in its raw state, it is completely decolourised, whilst the raw sample remains unchanged.

rapidly as possible, and the author has therefore examined the action of the agents in use or utilisable in the bleaching industry.

INVESTIGATIONS ON THE SAPONIFICATION OF FATTY BODIES ADHERING TO COTTON FABRICS.

"These fatty bodies include, beside those natural to cotton, all oils and fats introduced in manufacturing processes, such as olive, cotton-seed, palm, rape seed, and vegetable oils in general. The natural fats of cotton are more difficult to saponify than the oil, though not so difficult as tallow, which formerly was applied in the weaving, but is now for the most part replaced by mixtures of mineral and vegetable oils, which create greater difficulties in bleaching than tallow.

"*Preparation of Cotton Oil and Tallow.*—It is difficult to obtain these two bodies perfectly pure, but they can be freed from free fatty acids by repeated washings with boiling alcohol, and are then kept under a layer of alcohol, which immediately dissolves any glycerin and fatty acid formed by oxidation.

"*Method of Experimenting.*—Each experiment was done with two samples, 100 centimetres square (cut from an unbleached piece previously worked in boiling water), which were stained in their centre with a drop of the cotton-seed oil or fat from a glass rod. Samples with fat stains were heated to allow the fibre to absorb the fat. Experiments at 100° were performed in glass flasks, the amount of water being kept constant by additions.

"Experiments at 120° were carried out in iron tubes heated in an oil-bath. In these an ebullition occurred, as the crumpled samples plugged the tubes up, and almost prevented circulation. This will explain why in some cases the results obtained at 120° were not so good as those at 100°.

"After the boil, the samples were washed and dried and then put into cold water.

"A sample with all fat and oil removed is instantly wetted out (the place where the stain was cannot be recognised) and sinks.

"If any fat or oil remains, the sample wets out only slowly or is impermeable.

"A stain of tallow incompletely saponified will prevent wetting out, if the natural fats of cotton have been completely saponified on the remainder of the sample.

"When a fat fixed upon cloth has undergone a long boil, and only a little still remains in the interstices of the fibre, it will appear to thoroughly wet out, but it will show as a chalky or milky stain.

"Saponification should not be considered finished until all stain has disappeared.

THE TIME NECESSARY TO SAPONIFY THE NATURAL FATS OF COTTON AND TALLOW AT 100°.

CAUSTIC SODA LEY-BOIL.

5 grms. anhydrous caustic soda,	.	.	.	{ Saponification of the natural
1000 grms. water,	.	.	.	fats of cotton, . . . 18 hours.
				{ Saponification of tallow, . . . 34 "
10 grms. anhydrous caustic soda,	.	.	.	{ Saponification of the natural
1000 grms. water,	.	.	.	fats of cotton, . . . 18 "
				{ Saponification of tallow, . . . 34 "

SODA LEY-BOIL.

10 grms. Solvay soda,	.	.	.	{ Saponification of the natural
1000 grms. water,	.	.	.	fats, . . . 32 "
				{ Saponification of tallow, . . . 53 "
20 grms. Solvay soda,	.	.	.	{ Saponification of the natural
1000 grms. water,	.	.	.	fats, . . . 14 "
				{ Saponification of tallow, . . . 36 "

RESIN LEY-BOIL.

5 grms. anhydrous caustic soda,	.	.	.	{ Saponification of the natural	
2½ grms. resin,	.	.	.	fats,	. 18 hours.
1000 grms. water,	.	.	.	{ Saponification of tallow,	. 18 „
10 grms. anhydrous caustic soda,	.	.	.	{ Saponification of the natural	
2½ grms. resin,	.	.	.	fats,	. 6 „
1000 grms. water,	.	.	.	{ Saponification of tallow,	. 6 „
10 grms. soda,	.	.	.	{ Saponification of the natural	
2½ grms. resin,	.	.	.	fats,	. 36 „
1000 grms. water,	.	.	.	{ Saponification of tallow,	. 62 „

ALKALINE EARTH LEY-BOIL.

10 grms. caustic lime,	.	.	.	{ Saponification of the natural	
1000 grms. water,	.	.	.	fats,	. 6 „
				{ Saponification of tallow,	. 12 „
60 grms. barium hydrate,	.	.	.	{ Saponification of the natural	
1000 grms. water,	.	.	.	fats,	. 3½ „
				{ Saponification of tallow,	. 3½ „

“Baryta does not saponify to the bottom; where the stain of tallow is, the fabric instantly wets out, but water does not penetrate the spot. After boiling 18 hours it is no better. There then remains a slight residue of fat in the innermost parts of the fibre which baryta is unable to convert into soap.

“To estimate the action of the alkaline earths, which form insoluble soaps, the treated samples are passed through hydrochloric acid, and then boiled in three successive quantities of alcohol. The fatty acids in combination with the lime and baryta are thus liberated and removed from the fibre, leaving the neutral fats, which have withstood the action of the alkaline earths. By this means the extent of saponification is determined.

BLEACHING UNDER PRESSURE WITHOUT CIRCULATION AT 120°. TIME NECESSARY TO SAPONIFY FATTY BODIES.

CAUSTIC SODA LEY-BOILS.

5 grms. anhydrous caustic soda,	.	.	.	{ Natural fats of cotton,	. 4 hours.
1000 grms. water,	.	.	.	{ Tallow,	. 16 „
10 grms. anhydrous caustic soda,	.	.	.	{ Natural fats of cotton,	. 4 „
1000 grms. water,	.	.	.	{ Tallow,	. 16 „

CAUSTIC SODA AND RESIN LEY-BOIL.

5 grms. anhydrous caustic soda,	.	.	.	{ Natural fats of cotton,	. 4 „
2½ grms. resin,	.	.	.	{ Tallow,	. 8 „
1000 grms. water,	.	.	.		
10 grms. anhydrous caustic soda,	.	.	.	{ Natural fats of cotton,	. 4 „
2½ grms. resin,	.	.	.	{ Tallow,	. 8 „
1000 grms. water,	.	.	.		

CAUSTIC LIME LEY-BOIL.

10 grms. caustic lime,	.	.	.	{ Natural fats of cotton,	. 2 „
1000 grms. water,	.	.	.	{ Tallow,	. 4 „

BLEACHING AT 100°.—CLASSIFICATION OF THE RESULTS.

Quantities of the Reagents in a Litre of Water.	Time taken for Saponification.		Ratio of Time necessary for Saponification, taking as unit the time taken by Caustic Soda and Resin.	
	Natural Fats.	Tallow.	Natural Fats.	Tallow.
	Hours.	Hours.		
10 grms. anhydrous caustic soda, } 2½ grms. resin, }	6	6	1	1
60 grms. barium hydrate, . . .	3½	3½	0·6	0·6 maximum effect. 2
10 grms. caustic lime,	6	12	1	
5 grms. anhydrous caustic soda, } 2½ grms. resin, }	18	18	3	3
5 grms. anhydrous caustic soda,	18	34	3	5·7
10 grms. anhydrous caustic soda,	18	34	3	5·7
10 grms. Solvay soda,	32	58	5·3	10
10 grms. Solvay soda, }	36	62	6	10
2½ grms. resin, }				
20 grms. Solvay soda,	14	36
5 grms. Solvay soda, }	13	32
7½ grms. anhydrous caustic soda, }				

CONCLUSIONS DRAWN FROM THESE EXPERIMENTS AT 100°.

"Caustic soda saponifies the fats in half the time that soda does.

"There is little difference between the time taken by caustic soda of a strength of 5 grms. and 10 grms. per litre to saponify the fats. On the contrary, there is a great difference in the case of Solvay soda. Caustic soda, at 5 grms. per litre, and resin saponify the natural fats and tallow in 18 hours. At 10 grms. per litre, with the same amount of resin, one-third of that time only is taken.

"*Soda Ash and Resin*.—This mixture did not saponify the fats any quicker than without the addition of resin.

"*Caustic Lime*.—The natural fats were saponified in 6 hours and the tallow in 12 hours, at a strength of 10 grms. per litre.

"*Baryta*.—Saponification is attained in 3½ hours, but is not complete.

UNDER PRESSURE AT 120°.

"*Caustic Soda*.—With or without resin, saponification of the natural fats is effected in 4 hours. Without resin tallow requires above 12 hours for saponification, while with resin about 8 hours is sufficient. At 100°, with perfect circulation (the sample floating in the boiling liquid), saponification is much more rapid than at 120° without circulation.

"*Caustic Lime*.—At 10 grms. per litre, and without circulation, saponification of the natural fats takes less than 2 hours and tallow less than 4 hours.

"These samples, after the lime boil, were passed through hydrochloric acid, and then boiled in alcohol to remove fatty acid. If saponification had been incomplete, the alcohol would have left a residue of neutral fats unattacked on the fibre.

"*Conclusion.*—The action of circulation would then be of less importance in the lime boil than in the caustic soda and resin boil.

"These experiments on repetition have always given the same result in favour of the lime boil. Therefore, to obtain rapid and complete saponification, it is necessary to use the lime boil, or caustic soda and resin boil. If complete saponification is not essential, baryta can be used, requiring a very short time, but only carrying saponification to a certain point. It is necessary though with all alkaline earth leys to sour after, and use a second ley.

Baryta acts as a solvent of the colouring matter of cotton. Cloth boiled with it is much clearer than if boiled with lime.

"*Saponification of Cotton-seed Oil.*—A stain of cotton-seed oil placed on raw cotton cloth and boiled in soda ash, 10 grms. per litre, is completely saponified in 8 hours.

"The sample, on being placed on water, was impermeable, except where the stain of oil was, the water wetting this spot immediately.

"This shows that the cotton oil, in being saponified, removed the natural fats, which it covered, in 8 hours, and which, without its influence, had required boiling 32 hours.

"The two following experiments show (1) that this can also be applied to tallow ; (2) that oleic acid acts like the cotton-seed oil :—

"*Saponification of a Mixture of Tallow and Oleic Acid with Caustic Soda, and Cotton-seed Oil.*—The stains were made with the following mixtures.—1 part tallow, and 1 part oleic acid ; 1 part tallow, and 1 part cotton-seed oil.

"A sample with a stain of each of these mixtures was boiled with caustic soda, 10 grms. per litre. The stains were saponified in 10 hours. Thus, the presence of the fatty acid reduces the time taken to saponify tallow stains by two thirds. Stearic acid acts like oleic acid.

"*Saponification of Mixtures of Fatty Acids and Neutral Fats with Solvay Soda.*—Boil 1 hour, at 100°, in Solvay soda, 10 grms. to a litre of water.

"No. 1.—Stained with a mixture of 1 part tallow and 1 part stearic acid.

No. 2.—Stained with a mixture of 1 part cotton-seed oil and 1 part oleic acid.

"Result : No. 1.—On placing on water the stain is instantly wetted out ; No. 2.—The stain is instantly wetted out. Without the oleic acid, cotton-seed oil took 8 hours to remove. The general conclusion from these experiments, then, is that the presence of fatty bodies which are easily saponified greatly assists in the saponification of fats which resist the action of alkalies.

"*Saponification of Mixtures of Vegetable and Petroleum Oils.*—It is known that a stain of mineral oil is removed in bleaching if it is soaked with olive oil. A mixture of saponifiable fat and petroleum or shale oil leaves no trace after bleaching, whilst pure mineral oil is unaffected, and remains on the cloth.

"A mixture of five parts Scotch petroleum and five parts cotton, olive, or rape oil is removed with one lime boil for six hours at 120°, followed by a sour and ley boil of soda ash and resin for 10 hours at 120°, or by a simple ley boil of soda ash and resin alone for 10 hours at 120°, whilst a mixture of six parts Scotch petroleum and four parts vegetable oil (cotton, olive, or rape) offers so much greater resistance to bleaching that the mixture could not be used without injury to the material.

"The bleaching of stains of petroleum oil mixed with vegetable oil is only explained by a mechanical emulsive action which soap exercises upon hydrocarbons, and also on fats somewhat saponifiable.

"In order then to remove a stain of saponifiable neutral fat rapidly, it is necessary to use a soap capable of exercising an emulsive action, and a caustic alkali able to saponify the emulsified fats.

"In bleaching with soda or caustic soda without resin, the time is lengthened, because soap is formed in very small amount, and as fast as formed it is dispersed

in the ley, and becomes too diluted to act. However, by adding a little resin, a sufficient quantity of soap is formed to produce an emulsion of the fats.

"The author has found by experiment that larger amounts than $2\frac{1}{2}$ grms. resin per litre do not hasten saponification.

"The emulsive action is not then in a direct ratio to the amount of soap present, but reaches a maximum, which, however, can be altered to some extent by the quickness of the circulation.

"A body in movement in a liquid meets with resistance which varies according to the cube of its velocity. The emulsive power of a ley, which is only mechanical action, should vary then according to the cube of the velocity of the circulation.

"It is evident then that the speed of circulation in a bleaching system, where the neutral fats are acted on with caustic alkali and soap, is of great importance.

"*The Action of Lime on Mineral and Vegetable Oil Stains.*—A lime boil converts the vegetable oil in a mixed stain into soap, which forms fatty acid on souring. This fatty acid is removed as soap by soda and resin. To find whether the soap emulsifies, the oil stains were made with

6 parts Scotch petroleum,
4 parts vegetable oil,

and also with

6 parts Scotch petroleum,
4 parts oleic acid,

and the samples were boiled with soda ash and resin. Those made with the first mixture took the least boiling.

"It is thus shown that if instead of fatty acid a neutral saponifiable fat is present with mineral oil, the hydrocarbon is emulsified more rapidly.

"It would appear from this that the lime boil would hinder the removal of petroleum stains. Yet stains made with the first mixture were best removed by soda ash and resin after a lime boil and sour. Stains were removed in this way which perfectly resisted two or three boils with soda ash and resin. If a stain of a saponifiable fatty body is examined after liming, a rough deposit of lime soap is noticed on the cloth. This porous body may act on the hydrocarbon like pipe-clay or plaster, which are often used with success to remove grease stains. This fact should make the lime boil advantageous, as it should act as well on any fatty body which has escaped saponification as upon a mineral oil.

THE SAPONIFICATION OF FATTY BODIES BY SOLVAY SODA (ALMOST PURE CARBONATE), CAUSTIC SODA, AND VARIOUS MIXTURES OF THESE TWO.

"Leblanc soda, formerly used by all bleachers, was a mixture of carbonate and caustic soda, containing generally 20 per cent. caustic alkali. This salt gave a better white than Solvay soda. The theoretical conclusion drawn from this was that the quality of the white was owing to the amount of caustic soda in the ley.

"In order to find out whether a certain amount of carbonate of soda was advantageous, the author tried the experiments below, which seem to show that a ley of

$\frac{3}{4}$ caustic alkali, and
 $\frac{1}{4}$ carbonated alkali,

acts the best. The carbonate of soda may act somewhat like soap, as a weak emulsive agent.

"*Saponification at 100°.*—Time necessary to saponify tallow and the natural fats of cotton by mixtures of caustic soda and Solvay soda :—

20 grms. Solvay soda,	{ Saponification of the natural	
1000 grms. water,	fats,	14 hours.
					{ Saponification of tallow,	36 "
15 grms. Solvay soda,	{ Saponification of the natural	
$2\frac{1}{2}$ grms. anhydrous caustic soda,	fats,	12-14 "
1000 grms. water,	{ Saponification of tallow,	36 "

10	grms. Solvay soda,	{	Saponification of the natural	
5	grms. anhydrous caustic soda, .	{	fats,	12 hours.
1000	grms. water,	{	Saponification of tallow, .	32 ,,
5	grms. Solvay soda,	{	Saponification of the natural	
7½	grms. anhydrous caustic soda, .	{	fats,	10-12 ,,
1000	grms. water,	{	Saponification of tallow, .	26 ,,
10	grms. anhydrous caustic soda, .	{	Saponification of the natural	
1000	grms. water,	{	fats,	12-14 ,,
		{	Saponification of tallow, .	32 ,,

"Saponification of the Natural Fats of Cotton with Mixtures of Carbonate and Caustic Soda.—Boiled for eight hours at 100°. Amounts of alkali per litre :—

No. 1,	10	grms. Solvay soda.
No. 2,	{	8 grms. Solvay soda.
	{	1 gm. anhydrous caustic soda.
No. 3,	{	5 grms. Solvay soda.
	{	2½ grms. anhydrous caustic soda.
No. 4,	{	3½ grms. anhydrous caustic soda.
	{	2 grms. Solvay soda.
No. 5,	5	grms. anhydrous caustic soda.

"Results.—The samples boiled in No. 4 were the only ones which thoroughly wet out; those in No. 5 wet with difficulty, while in No. 1 they were perfectly impermeable. No. 3 gave results similar to No. 5. These experiments fully confirm the results of preceding ones.

"The Saponification of Fats by means of Caustic Lime.—When the soda ash boil immediately follows the lime boil, as in Dana's process, soda soap and carbonate of lime are formed. If the lime saponification has been incomplete, after all lime soap is decomposed, a residue of natural fat remains on the fibre, which will be saponified by the influence of the soap present. By Scheurer-Rott's process of souring after liming, if the lime saponification is incomplete, the free fatty acid formed in souring will assist in the saponification of any residue of neutral fat. Therefore, to ascertain if the lime saponification has been complete, after souring with hydrochloric acid, the sample is washed with alcohol, which dissolves the free fatty acid, and leaves the neutral fats. If now, after drying, the sample wets out entirely, the lime saponification has been complete, but if it does not take up water, a residue of unsaponified neutral fat is present.

"By this means the time necessary for the lime saponification of neutral fats can be determined, and also what action soap and fatty acids have on these fats.

"Saponification of the Natural Fats of Cotton with Caustic Lime at 100°.—The ley contained 10 grms. caustic lime in 1,000 grms. water. The duration of the ley-boil for complete saponification depends on which of the three treatments below follow:—

"1. Souring in hydrochloric acid, washing in boiling alcohol.

"2. Boiling 1 hour in soda at 10 grms. per litre without souring.

"3. Souring and boiling 1 hour in soda at 10 grms. per litre.

"By the first treatment the time necessary for entire saponification of the natural fats with lime is determined.

"By the second the proportion of soap to be formed by double decomposition of the lime soap and soda needed to saponify the residual fat is determined.

"No. 3 will show to what extent the free fatty acid assists in saponifying the same residual fat.

"The author found that to obtain satisfactory saponification, the first treatment requires a lime boil of six hours, the second treatment a lime boil of four hours, and the third a lime boil of one hour. The great advantage of souring after the lime boil is manifest.

"With tallow there are not such great differences. The first treatment requires a lime boil for ten to twelve hours, and the third a lime boil for four to six hours.

"The conclusion from these experiments seems to be that if one half of a fatty body is saponified by the lime boil, by souring and boiling in soda the whole of it is saponified. This fact confirms the rule formed previously, that fatty acids and neutral fats which are easily saponifiable assist the saponification of bodies not easily saponified.

"*The Action of the Lime Boil under Pressure.*—It has been shown that at 120° the natural fats of cotton are saponified in less than two hours by the lime boil, and tallow in four hours. This is very remarkable, since caustic soda and resin at the same temperature take eight hours.

"It shows that the action of caustic soda and resin soap, without circulation at 120°, would be no better than at 100° with good circulation. Circulation accelerates saponification, because to emulsify fatty bodies with soap, motion is necessary. Therefore, to obtain as rapid saponification with caustic soda and resin as with lime, circulation must be perfect.

"The remarkable action of lime upon the neutral fats at 120° is the more inexplicable, as caustic lime is least soluble in water at high temperature. At 15° water dissolves 1.778 grms. of caustic lime, and at 100° only 1.127.

"In bleaching with good circulation, one would expect the lime precipitated by the rise of temperature to accumulate on the top of the pieces near the outlet. This is not found to be the case. The ley remains perfectly clear. At the end of the boil, the pieces are uniformly impregnated with caustic lime, removed with difficulty by the cold water washing. When the wash-water is no longer dirty, the pieces are still strongly alkaline, red litmus being turned blue when it is left in contact with the fibre. These facts seem to show that lime is not precipitated in the surface of the cloth simply, but that the caustic lime has really mordanted it.

"The following experiments confirm this opinion:—

"*Examination of the Lime Ley.*—A sample of lime ley withdrawn from a pressure kier at the end of the boil was almost clear, and on filtering left a negligible quantity of insoluble matter in the filter. On titrating, a little more than 1 gm. free caustic lime per litre was found in it. When introduced into the kier, the ley contained 8 to 9 grms. per litre. About 7 grms. then is either fixed on the cloth or left in the ley as carbonate of lime.

"*Analysis of the Ley.*—100 kilos. of lime ley were evaporated to a paste, weighing 7.4 kilos. and containing 3.5 kilos. dry matter at 100°, and leaving on incinerating 800 grms. ash, consisting of carbonate of lime and a little alumina and iron.

"Its composition is then

Water,	96.5 per cent.
Organic matter,	3.0 "
Caustic lime,	0.5 "

"The ley, therefore, contains 5 grms. lime per litre, of which 4 grms., or a little less, is present as carbonate of lime.

"*Examination of Pieces after the Lime Boil.*—When the sample of ley was withdrawn, three samples were taken out of the kier from different places, strongly pressed, dried, and portions incinerated.

No. 1 left an ash of	3.14 per cent.
No. 2, ,, ,,	3.11 "
No. 3, ,, ,,	3.15 "

"Other portions, after souring, left, on calcining, 0.258 per cent. ash, the difference $3.14 - 0.258 = 2.88$ per cent., representing the lime retained by the fibre, expressed as carbonate, $2.88 \text{ Ca C O}_3 = 1.06 \text{ Ca O}$. From these experiments it appears that the cloth has absorbed $\frac{1}{2}$ to $\frac{2}{3}$ of the amount of lime in the ley, which probably, therefore, hastens the saponification of fatty bodies.

"A high temperature is, therefore, advantageous in saponifying fats, as the higher the temperature the more lime is taken up by the cloth.

"From his experiments the author gives the following as practical processes for the removal of fatty matters from cotton:—

"1. A single ley boil with caustic soda and resin soap.

"2. A lime boil, followed by a sour and a soda ash ley boil.

"The first process can now be carried out by the use of the now well-known kier of Mather & Platt, which the author considers has great advantages over the old kier, mainly owing to its mechanical improvements, but that the second process from its reliability and elasticity is not likely to become obsolete.

"*The Action of Metallic Mordants in Bleaching Operations.*—Samples of cotton were mordanted with

Pyrolignite of iron.

Acetate of alumina.

„ lead.

„ tin.

„ magnesia.

Ferric acetate.

With lime boiled under pressure the magnesia was completely removed, and only a trace of lead was left, but the Fe O , $\text{Fe}_2 \text{O}_3$, Sn O_2 , and $\text{Al}_2 \text{O}_3$, had more or less resisted the lime boil. This was ascertained by dyeing in alizarin after the lime boil, and comparing with samples dyed without being lime boiled.

"The amount of mordant retained was least in the case of bleached cotton, greater with bleached cotton prepared with sulpholeate of soda, and with unbleached cotton, and greatest with bleached cotton oiled by the old Turkey-red process.

"Souring removed all the oxides except Sn O_2 .

"By boiling with soda ash and resin for 10 hours under pressure, all mordants except iron were totally removed."

OTHER BLEACHING PROCESSES.

The processes described are those which may be said to be in general use at the present time. Within the last ten years several other processes have been proposed which differ more or less from the older processes in principle. Some of these have been carried out on the large scale with more or less success. Undoubtedly the most important, and the one which has met with the greatest commercial success, is that devised by M. Horace Koechlin, and carried into practice in the steamer kier specially constructed for the purpose by *Messrs. Mather & Platt*.

In this system, the lime boil is entirely dispensed with, and this, as well as the two ley boils of the old process, are replaced by a single ley boil in caustic soda and resin soap. The kier in which the ley boil is effected is shown in section and longitudinal section in Figs. 35 and 36. It consists of a huge wrought-iron horizontal egg-ended cylinder, provided at one end with a lid or door. When lowered the wedge-shaped door fits into a frame wedging itself steam tight. The raising and lowering of the door is done by means of a hydraulic ram.

The goods are packed evenly in waggons, which are made of galvanised sheet-iron and provided with false bottoms, and which are usually so constructed that two fit into a kier.

The waggons having been run in, the kier is closed, the air expelled by the admission of steam, and a solution of caustic soda caused to shower over each waggon by means of the centrifugal pump, P, through the pipe, B, which divides at D. After percolating through the goods, the liquor collects beneath the false bottom of each waggon and is drawn thence through the pipe, T, through the centrifugal

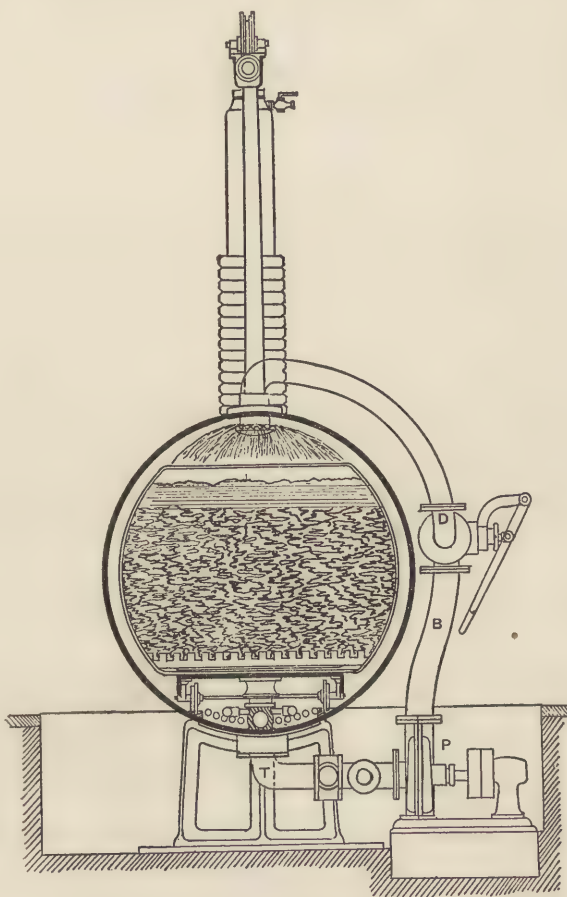


Fig. 35.—The Mather kier. Section.

pump again, a continuous circulation thus being brought about. The circulating liquor in the kier is heated by a coil pipe laid in the bottom, the condense water from which is drawn off outside so as not to dilute the liquor. There is also a perforated pipe to boil by direct steam, if necessary.

When the waggons have been run out, fresh ones are ready to take their place, and thus a great saving in time is effected.

The chemicking, souring, washing, &c., which follow the treatment in the steamer kier may be carried out as in the ordinary bleaching process.

The kier may also serve for boiling with lime, and is sometimes used for this purpose in bleaching "back greys" which have been used in calico printing.

The time required for a full bleach by this method is twenty-six

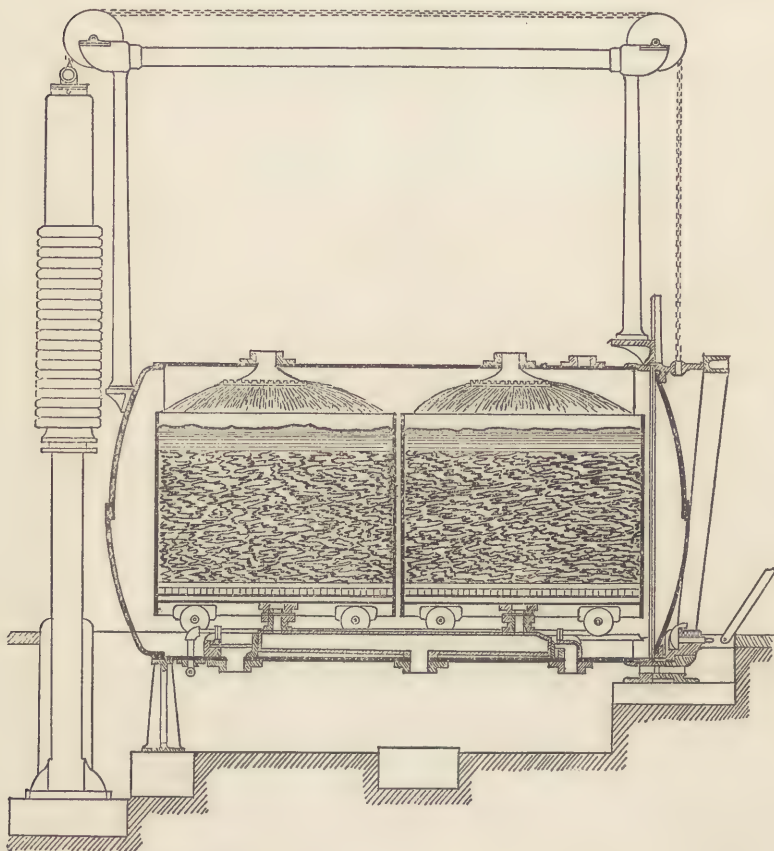


Fig. 36.—The Mather kier. Longitudinal Section.

hours. The largest kier made is capable of holding 3·3 tons of cloth, and is capable of turning out regularly thirty tons of bleached calico per week. The main advantages of the kier are a saving in water, power, time, labour, and fuel, while at the same time the number of operations is reduced, and with these, the wear and tear to which the pieces are otherwise subjected in the bleach-house are done away with.

According to a private communication from M. H. Koechlin, the

following is the *modus operandi* at present employed in the works at Loerrach :—

The grey pieces are passed through sulphuric acid at 2° to 8° Tw., and left in the acid 10 to 12 hours, after which they are washed and passed at 75° C. through

1800 litres water,
25 kilos. caustic soda, 72 per cent.,
5 litres bisulphite of soda, 64° Tw.,

for every 250 pieces of 100 metres each. They are then packed evenly

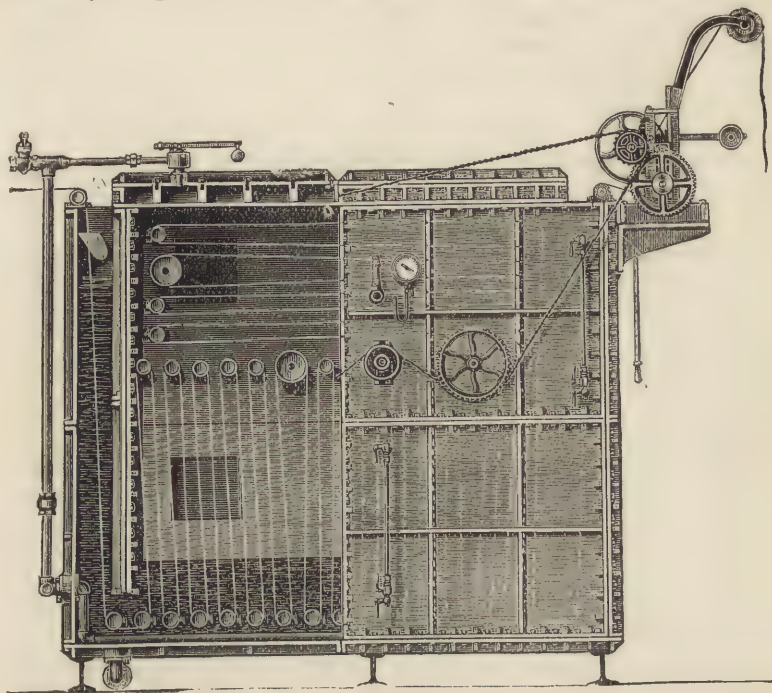


Fig. 37.—Grether & Bentz's bleaching kier.

in the waggons and run into the kier. Here they are treated for eight hours (under 7 to 15 lbs. pressure) with a solution of

2000 litres water,
30 kilos. caustic soda,
40 „ soda ash,
20 „ resin.

Wash in kier 4 to 5 times with cold water. Then circulate a solution of bleaching powder made up from

2000 litres water,
100 „ chloride of lime solution at 12° Tw.,
2 „ hydrochloric acid.

Allow to circulate five hours. Wash in kier, pass through sulphuric acid at 2° to 8° Tw., wash in washing machine, and dry.

According to another system recently proposed by *Messrs. Grether & Bentz*, for which a machine has been constructed by *Messrs. Edmeston & Sons* of Manchester, the operation of boiling with alkali is rendered continuous.* The machine constructed for this purpose consists of a rectangular iron tank provided at each end with a partition which reaches nearly to the bottom. These partitions dip beneath the surface of the liquid and act as water seals for the interior air-tight compartment.

The working of the kier will be readily seen from the figure, in which part of the side is removed in order to show the internal arrangement of the rollers. The pieces pass in underneath the first partition and over a number of rollers through the boiling alkali, thus traversing the upper part of the kier several times horizontally, and ultimately passing out beneath the second partition or water seal. They are thus subjected to the action of the boiling alkali and soap in the lower part, and to the action of steam under a slight pressure in the upper part of the kier. The pressure in the interior will depend upon the difference in height of the levels of the liquid on either side of the partitions. The pieces pass through at the rate of 30 yards per minute.

The Mather-Thompson Continuous Bleaching Apparatus effects the further treatment of the goods after they have been boiled with caustic soda in the Mather kier. It contains 15 partitions in which the chemicking treatment with carbonic acid, washing, and souring are effected. In the first partition, the pieces are simply run through warm water; in the second, they pass through chloride of lime at 2° Tw. The third partition is a chamber filled with carbonic acid gas, the pieces passing in and out through narrow slits. In the fourth, fifth, and sixth partitions they are washed with cold water; in the seventh they pass through a soda solution (1 grm. per litre) at 60° to 75° C; in the eighth, ninth, and tenth they are washed again with water. In the eleventh partition they are again passed through chloride of lime, this time at $\frac{1}{2}$ ° Tw. The twelfth is a second carbonic acid chamber, and the thirteenth, fourteenth, and fifteenth contain weak hydrochloric acid (1 per cent. solution). After leaving the apparatus, the goods are washed in an ordinary washing machine, and dried.

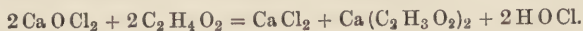
The specialty in the Mather-Thompson process is the use of carbonic acid after the chloride of lime, the effect of which is, as has been pointed out before in the description of the ordinary bleaching process, to liberate the free hypochlorous acid on the fibre, and thus accelerate the bleaching action. The pieces pass through the whole apparatus in about three minutes, and it is possible, according to J. Heilmann,† to get through as much as 5 tons in a working day of ten hours. Besides this enormous saving in time, there is said to be a great saving in materials, while the bleaching is effected as well and

* *The Dyer and Calico Printer*, February, 1891.

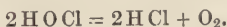
† *Textile Man.*, 1886.

as thoroughly as in the older processes. But, in spite of all these advantages, it is a curious fact that only one firm in England (Messrs. Ainsworth & Co., in Bolton) is using this apparatus at the present time.

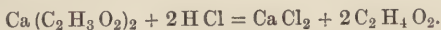
Lunge's Improvements in Bleaching consist in the use of acetic acid along with the bleaching powder. Free hypochlorous acid is thus liberated, according to the equation—



The free hypochlorous acid, in acting on the constituents of the cotton, gives up its oxygen; and free hydrochloric acid results:



The free hydrochloric acid resulting from this decomposition is just sufficient to liberate the acetic acid again from the calcium acetate formed in the first instance:



The process thus becomes continuous, and a given amount of acetic acid suffices to decompose a very large quantity of bleaching powder. The subsequent treatment with acid is rendered unnecessary and the expense and time of one operation are thus saved.

Use of Free Oxygen.—Free oxygen used in conjunction with chloride of lime is said to have given much better results in the bleaching of paper pulp than chloride of lime alone; but no results of experiments on textile materials have hitherto been published.

The Hermite Bleaching Process.—The bleaching liquor employed in this process is produced by the electrolytic decomposition of solutions of the chlorides of aluminium, calcium, or magnesium, preferably the latter.*

BLEACHING WITHOUT CHLORINE.

The use of chlorine for calico bleaching is not altogether indispensable. Cotton freed from the natural impurities soluble in alkalis and acids is bleached if exposed to light for a sufficient length of time. However, this process, although used to some extent in linen bleaching, is seldom adapted to cotton as it takes too long, and would be too cumbersome for large quantities.

Bleaching with Peroxide of Hydrogen.—This bleaching agent would, no doubt, rapidly supersede the use of chloride of lime in the bleaching of calico if its price were to come down sufficiently low, since it produces a better white. The best results are obtained with it by means of the method proposed by Horace Koechlin.

For five pieces of 100 metres each, or about 50 kilos. of cotton, prepare a bath with—

* For further information on this subject see F. Hurter's paper "On Hermite's electrolytic process for the manufacture of bleaching liquor," *Journ. Soc. Chem. Ind.*, 1887, p. 337.

Water,	100 litres.
Caustic soda,	10 kilos.
Soap,	30 „
Calcined magnesia,	5 „
Peroxide of hydrogen of 12 volumes strength,	50 litres.

Boil the goods in this solution for 6 hours, wash, pass through sulphuric acid at 3° Tw., and wash again.

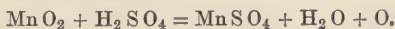
If the calcined magnesia is not added to the bath the decomposition of the peroxide takes place so rapidly that the oxygen generated has not time to take effect. Its action in retarding the evolution of the oxygen is due, according to Prudhomme*, to the formation of a hydrated peroxide of magnesium corresponding to the formula $(3 \text{ Mg (O H)}_2 + \text{Mg O}_2)$ or $(3 \text{ Mg (O H)}_2 + \text{Mg O (O H)}_2)$, which decomposes very slowly at the boiling temperature.

The magnesium soap which forms during the boiling is not of a sticky nature and is easily removed from the pieces by washing in water.

Bleaching with Permanganate of Potash.—Permanganate of potash is a powerful oxidising agent, and, as such, is capable of destroying the natural colouring matter of cotton. As in bleaching with chlorine, it is necessary to remove the grease and wax-like impurities by boiling with alkalis, previous to bleaching. The method usually recommended is to steep the cotton thus prepared in a neutral, or slightly acid, solution of permanganate of potash (commercial manganate of soda would probably do as well and would be much cheaper). Alkaline solutions must be avoided since they rapidly disintegrate the fibre, oxycellulose being formed. When taken out, the cotton is of a more or less dark brown colour, due to the reduction of the permanganate and the consequent deposition of peroxide of manganese on the fibre. This can be instantly and completely removed by passing the cotton through a solution of sulphurous acid or bisulphite of soda.

By this process, part of the available oxygen originally contained in the permanganate is lost in the peroxide which deposits on the fibre. In order to obtain the complete effect of the available oxygen, Manzoni † proposes the following method:—

The cotton yarn is freed from grease and wax-like impurities by boiling in a solution of caustic soda (4 grms. per litre) under two atmospheres pressure. It is then well washed and steeped for 5 hours in a solution of sulphuric acid at 7½° Tw., to which the permanganate is added in concentrated solution in two or three different portions. Under these conditions, the yarn does not turn brown, the acid being strong enough to decompose any peroxide of manganese which might form, according to the equation—



The operation being carried out in the cold, no tendering of the fibre takes place; but it is necessary to wash well as soon as the cotton

* *Journ. Soc. Dyers and Col.*, 1891.

† *Ib.*, 1889, p. 98.

is taken from the bleaching bath. Manzoni points out that in working by this method, a much smaller amount of permanganate is necessary than is generally given in text-books or manuals; he finds that half a kilo. of permanganate is sufficient to produce a good ordinary white on 100 kilos. of cotton yarn.

Bleaching with Calcium Sulphite and Caustic Soda.—According to Horace Koechlin, an excellent white may be produced on cotton piece goods by the following simple process:—The pieces are impregnated with a mixture of milk of lime and sulphite of soda (which by double decomposition would form calcium sulphite and caustic soda), steamed for one hour, washed, passed through acid, and washed again.

LINEN BLEACHING.

As has already been pointed out in the description of the fibres, the raw linen fibre contains a much larger amount of foreign substances than cotton. While ordinary raw cotton only contains about 5 per cent. of foreign matter, the loss in weight of linen during the bleaching process amounts to 25 to 30 per cent. The nature of the foreign substances (other than cellulose) contained in the raw flax seems to have been but imperfectly studied; all that we know is that it contains, besides a wax-like substance, so-called pectic matters, which can be removed by prolonged treatment with alkalis. But linen is more easily affected by alkalis, acids, and chlorine than cotton; and the bleaching of linen is, therefore, a longer and more tedious process than the bleaching of cotton. A severe treatment would either result in the tendering of the fibre or in "setting" the colour, and when this latter fault has once shown itself it is difficult to deal with. The general treatment of linen, either in the yarn or in the piece, is similar to that adopted for cotton; but the reagents are weaker, and it is necessary to repeat some of the operations several times before a satisfactory white is obtained.

A special operation necessary in linen bleaching, but not used for cotton, is the "grassing," a remnant of the old method of bleaching which was in use before the introduction of chlorine as a bleaching agent. In grassing, the yarns or pieces are exposed in fields, after treatment with alkali and acid, to the joint action of light, air, and moisture. In dry weather the goods are sprinkled with water from time to time. The effect of grassing is considered to be due to the action of the ozone and peroxide of hydrogen which are usually found in small quantities near the ground.

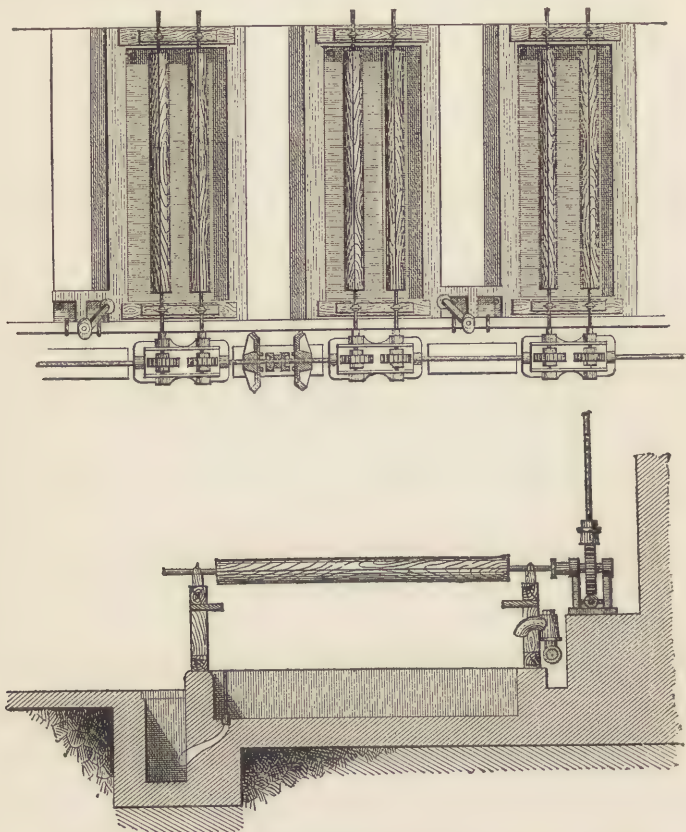
LINEN YARN.

The bleaching of linen yarn is similar in principle to the bleaching of cotton, but the process lasts longer, if a full bleach is required. This

is, however, not always necessary. For some purposes a ley-boil and subsequent treatment with acid suffices, while, in other cases, the yarn is required quarter bleached, half bleached, or three-quarters bleached. As the white increases in purity, the strength of the yarn is diminished.

The following is, according to Hummel,* a brief description of the method generally adopted in Ireland:—

1. *Ley-Boil*.—Boil for 3 to 4 hours with 10 per cent. soda ash in low-pressure kiers.



Figs. 38 and 39.—Haubold's reeling machine for linen yarn.

After the ley-boil, the yarn is washed, either by hand or machine, and squeezed.

2. *Treatment with Chloride of Lime*.—The yarn is reeled for one hour in chloride of lime solution at $\frac{1}{2}^{\circ}$ Tw. Chloride of soda or chloride of magnesia are frequently preferred to chloride of lime, as they form no insoluble carbonates in the fibre and the subsequent sour can be used much weaker.

* *Dyeing of Textile Fabrics*, p. 86.

The reeling, which is also a specialty in linen bleaching, is effected in shallow stone, cement, or wooden troughs, of which one is shown in section and three in plan in Figs. 38 and 39.

The reels receive an alternating backward and forward motion from the main shaft. When the operation is over they are removed and replaced by another lot, freshly filled. During the operation, only a small portion of the yarn lies beneath the surface of the liquid, the rest being exposed to the air, the carbonic acid of which liberates free hypochlorous acids from the bleaching liquor and thus assists materially in the bleaching.

3. *Sour* by steeping for one hour in sulphuric acid at 1° Tw. Hydrochloric acid would be preferable to sulphuric acid, since the calcium chloride formed is readily soluble, while calcium sulphate is not. After souring, wash.

4. *Scald*.—Boil for an hour with 2 to 5 per cent. soda ash. Wash.

5. *Reel* for one hour in chloride of lime at $\frac{1}{2}$ ° Tw. Wash.

6. *Sour* for one hour in sulphuric acid at 1° Tw. Wash. At this stage the yarn is half-bleached. For a three-quarters bleach, the yarn is again boiled with soda ash, exposed in fields for about a week, steeped in very dilute chloride of lime for 10 to 12 hours, soured and washed. For a full bleach these latter operations are repeated two or three times, the concentration of the solutions being diminished for each successive treatment.

LINEN PIECES.

As is the case in the bleaching of cotton pieces, the methods in general use, although based upon the same principles, may vary considerably with regard to detail. This will be seen by a comparison of the following processes. The first is a short account (according to Ganswindt) of the process adopted at present by a large Silesian bleachworks.

The pieces are trodden down evenly in a large wooden tub with pure river water heated to 44° C. When the cask is filled, it is covered up and left to itself. A fermentation soon sets in, which lasts about 36 hours. The pieces are taken out, rinsed, and exposed or grassed for 2 to 3 days, then dried. By this treatment the linen loses 10 to 15 per cent. in weight.

Then follows the first ley-boil in low-pressure kiers or casks with false bottoms, let into the ground, with a 1 per cent. solution of soda ash. The pieces are now again exposed for 2 to 3 days, after which follows the second ley-boil, and grassing again for 2 to 3 days. These operations are repeated up to the eighth ley-boil, the strength of the ley slowly decreasing for each successive boil from 1 kilo. to 0.55 kilo. for each 100 litres of water.

After the eighth ley-boil, the goods are rinsed and soured by steep-

ing for 5 to 8 hours in dilute sulphuric acid (1 pt. strong sulphuric acid to 200 pts. water), after which they are well washed.

They are then passed into a bath of chloride of lime containing 1 pt. bleaching-powder dissolved in 600 litres water, in which they are allowed to remain for 6 to 8 hours.

Then follows a second sour like the first.

After well washing, the pieces are slowly heated from 45° to 75° C. with a solution containing in 600 litres of water $2\frac{1}{2}$ kilos. white curd soap and 1 kilo. soda ash, and then exposed for 2 to 3 days.

At this stage the goods undergo another operation, which is a

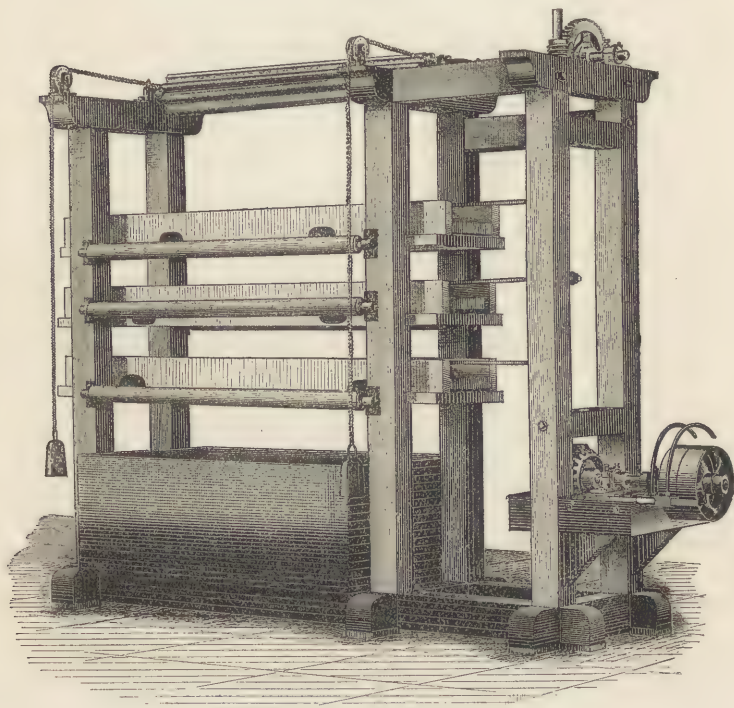


Fig. 40.—Rubbing boards for linen pieces.

specialty in linen bleaching, viz., “rubbing,” the object of which is to remove by mechanical means small black specks or “sprints” which still adhere to the material. This is effected in the machine shown in Fig. 40 (Haubold).

It consists of a wooden framework provided with three pairs of rubbing boards, underneath which there is a wooden vessel in which the pieces are steeped in a strong soap solution. Of each pair of rubbing boards, the lower one is rigid, while the upper one receives by a crank, not shown in the figure, a to and fro motion. The pieces are drawn through the rubbing boards by means of a pair of

fluted rollers at the top of the machine. The pressure of the fluted rollers is regulated by weights. The rubbing is continued until the black or yellow stripes or sprits are removed.

After this treatment, the goods are again treated with soda solution (0.25 kilo. to 100 litres of water), beginning at 45° and gradually raising the temperature to 80° C. They are then grassed again for 2 days and washed.

This is followed by a second treatment with chloride of lime, which is effected like the first. Wash.

The goods are then soured again as above, and, after washing, are heated slowly from 45° to 70° C. with water containing in 300 litres 0.5 kilo. soda ash and 1½ kilos. white curd soap. Expose again in fields for 2 days, and wash.

At this stage a sorting of the pieces takes place. Those which show a satisfactory white are blued and finished.

Those which are not satisfactory are treated again in the rubbing boards, then heated as in a previous operation with soda solution (0.25 kilo. to 100 litres of water) from 45° to 80° C., and grassed for two days. Those which now show a satisfactory result are soured, washed, dried, and finished. The rest are steeped again in chloride of lime, soured, treated again with alkali, grassed, washed, blued, and finished.

Hummel* gives the following *résumé* of a modern Irish process for 1500 kilos. brown linen, handkerchiefs, &c., with low-pressure kiers:—

1. *Lime-boil*.—125 kilos. lime, boil 14 hours; wash 40 minutes in stocks.

2. *Sour*.—Hydrochloric acid 2½° Tw., steep 2 to 6 hours; wash 40 minutes in stocks; “turn hank,” and wash 30 minutes in stocks.

3. *Ley-boils*.—1st, 30 kilos. caustic soda (solid), 30 kilos. resin, previously boiled and dissolved together in water; 2,000 litres water; boil 8 to 10 hours, run off liquor and add. 2nd, 15 kilos. caustic soda (solid) dissolved in 2,000 litres water; boil 6 to 7 hours; wash 40 minutes in stocks. (See *Bleaching of cotton yarn*.)

4. *Expose in field* 2 to 7 days, according to the weather.

5. *Chemick*.—Chloride of lime solution ½° Tw., steep 4 to 6 hours; wash 40 minutes in stocks.

6. *Sour*.—Sulphuric acid 1° Tw., steep 2 to 3 hours; wash 40 minutes in stocks.

7. *Scald*.—8 to 13 kilos. caustic soda (solid) dissolved in 2,000 litres water, boil 4 to 5 hours; wash 40 minutes in stocks.

8. *Expose in field* 2 to 4 days.

9. *Chemick*.—Chloride of lime solution ¼° Tw., steep 3 to 5 hours; wash 40 minutes in stocks.

The goods are examined at this stage; those which are sufficiently

* *The Dyeing of Textile Fabrics*, p. 88.

white are soured and washed, and those which are not are further treated as follows:—

10. *Rub with rubbing boards* and a strong solution of soft soap.

11. *Expose in field* 2 to 4 days.

12. *Chemick.*—Chloride of lime solution $\frac{1}{8}^{\circ}$ Tw., steep 2 to 4 hours; wash 40 minutes in stocks.

13. *Sour.*—Sulphuric acid 1° Tw., steep 2 to 3 hours; wash 40 minutes in stocks.

“Turnhanking” consists in loosening the entangled pieces and re-folding them, so that every part may be exposed to the action of the hammers in the wash stocks.

The following is, according to Herzfeld,* another Irish process, in which the bleaching is effected without the aid of grassing:—

1. *Steeping.*—The goods are steeped for 36 hours in a solution of potash or soda ash at 1° Tw. Wash.

2. *First Ley-boil.*—Boil for 6 to 10 hours in a solution containing $\frac{3}{4}$ kilo. to every 100 litres of water. In place of caustic soda, a solution of resin soap, containing $1\frac{1}{2}$ kilos. resin and $1\frac{1}{2}$ kilos. caustic soda in every 100 litres, is sometimes employed. Its action is milder than that of the caustic soda. Sometimes it is necessary to repeat the boiling with resin soap.

3. *First Treatment with Chloride of Lime.*—The pieces are steeped for 10 to 15 hours in a solution of chloride of lime at $\frac{1}{2}^{\circ}$ Tw., and washed.

4. *Sour.*—Steep for 3 to 6 hours in sulphuric or hydrochloric acid at $\frac{1}{2}^{\circ}$ Tw., and wash.

5. *Second Ley-boil.*—Boil for 4 to 5 hours in a solution of caustic soda containing 0.5 to 0.6 kilo. solid caustic per 100 litres. Wash.

6. *Second Treatment with Chloride of Lime.*—Steep for 10 to 14 hours in a solution of chloride of lime at $\frac{1}{4}^{\circ}$ Tw.

7. *Sour* as above (4).

At this stage the goods are examined. Those pieces which show a satisfactory result are washed, blued, and finished. The rest are subjected to the following treatment:—

8. *Rub*, in rubbing boards with a strong solution of soft soap, and wash.

9. Steep in chloride of lime solution at $\frac{1}{4}^{\circ}$ Tw.

10. Sour, wash, blue, and finish.

The white obtained by this process is, as a rule, inferior to that obtained by processes in which grassing is used.

Ganswindt† recommends the following process for 1,000 kilos. linen:—

First Ley-boil.—75 kilos. burnt lime slaked. Boil 12 hours in kier. Wash $\frac{1}{2}$ hour.

* *Das Färben und Bleichen d. Textilfasern*, vol. ii., p. 171.

† *Handbuch der Färberei*, p. 375.

First Sour.—Hydrochloric acid at 3° Tw. Steep for several hours. Wash for 1 hour.

Second Ley-boil.—20 kilos. resin dissolved in 20 kilos. caustic soda and made up to 1,500 litres. Boil 6 hours, wash 1 hour.

First Chloride of Soda Bath.—Chloride of soda (sodium hypochlorite) at $\frac{3}{4}$ ° Tw. Saturate, squeeze, and pass through a chamber filled with carbonic acid gas.

Fourth ley-boil with 1,500 litres water only. The sodium carbonate formed by passing the goods impregnated with chloride of soda through the carbonic acid gas renders any further addition unnecessary.

Second chloride of soda bath as the first. Pass again through carbonic acid gas.

The boiling with water, treatment with chloride of soda and carbonic acid are repeated until a satisfactory white is obtained.

Within recent years the Mather & Platt bleaching kier has been employed with success in the bleaching of linen.

The ordinary bleaching process for linen pieces occupies from 3 to 6 weeks. For densely woven material the yarn is sometimes partially bleached before weaving.

Bleaching with Permanganate of Potash.—This reagent has been proposed for the bleaching of linen yarns and pieces by Tessié du Motay. The goods, after having been subjected to fermentation, are steeped for 15 to 20 minutes in a solution of permanganate of potash (4 to 6 per cent. of the weight of the material) and magnesium sulphate or chloride. They are then decolorised by being passed through sulphurous acid or an acidulated solution of peroxide of hydrogen. These operations are repeated until a satisfactory white is obtained.

The process is said to be used with great success in works in France. By means of it yarns are said to be bleached in one day, pieces in three days (*Ganswindt*).

Manzoni's method as proposed for cotton (see p. 110) would probably also give good results on linen.

BLEACHING OF HEMP.

A full bleach on hemp is seldom desired, although this can be effected by processes similar to those adopted for linen. At the Paris Exhibition of 1889 there were several exhibits of beautiful white hempen fabrics, which strongly resembled linen in appearance.

For string and light ropes a rough bleach is sometimes employed. For this purpose the goods are first boiled for half an hour in a solution of 10 kilos. silicate of soda at 70° Tw. in 500 litres water. They are then boiled in water alone, after which they are rinsed and steeped for 24 hours in a solution of 10 kilos. bleaching-powder in 1,500 litres water. After being allowed to drain they are hydro-extracted and soured in hydrochloric acid (1 litre commercial hydro-

chloric acid in 1,000 litres water). They are then well washed in water, and dried. A better white is obtained by repeating these processes.

BLEACHING OF JUTE.

Although the jute fibre, with respect to its modes of manufacture and commercial applications, has advanced with such rapid strides since first brought before the manufacturing community, yet, as regards its bleaching, the success does not appear to have been so marked; for there is little doubt that, to a large extent, the same processes are still carried out as were in operation when first it became of commercial importance. Probably this may be accounted for by the fact, that it is not necessary for the bleached fibre to have such a degree of purity as is required, for example, in the case of flax or cotton, for, whereas with the latter it is essential for the production of delicate shades of colour, with jute, sufficient delicacy can be obtained from either the cream or light straw-coloured material.

After bleaching it is divided, broadly speaking, into two classes according to the final shade required on the yarn, one being known as the "Half Bleach," and the other as the "Full Bleach." The former is a straw, and the latter a light cream colour, this difference being utilised principally in the subsequent dyeing operations, as, for all purposes where dark shades are required, either the raw or "Half Bleach" is invariably used, whereas for light shades the "Full Bleach" quality is necessary.

In comparison with the processes carried out for the bleaching of cotton, those of jute are very inferior indeed; for, although both may be contaminated with natural impurities to the same extent, which impurities must be removed during bleaching, those of jute are removed quicker and with less regard to the ultimate nature of the fibre, than those of cotton.

Bleaching of Jute Yarn.—The following is an outline of the general method of bleaching jute yarn at present carried out in the Dundee district.

First Method.—The hanks are sorted into bundles of from 6 to 8 cwts. each, according to the size of the vessel, then suspended on smooth wooden rods, and immersed in a rectangular tank filled with water containing the necessary amount of bleaching-powder solution. Each separate rodful of yarn is taken, swayed once or twice to and fro, and then carefully lifted, so that the exposed portion of the yarn may easily be placed in the liquid. This lifting is performed either by the workmen, or preferably by an arrangement of levers, whereby the whole of the yarn is immersed in the bath and easily moved therein without any portion becoming exposed to the air. After remaining in this bath for 1 hour, at a temperature of 80° to 100° F. (27·7° to 37·7° C.), the liquid is run off and the hanks allowed to drain. They are then

washed and placed in a similar tank containing dilute sulphuric acid, from which, after remaining a quarter to half an hour, they are withdrawn, and again well washed in successive quantities of water.

Quantities of Materials, &c.—Yarns, 6 cwts.; bleaching-powder solution, 8° Tw., 120 gallons; temperature, 100° F. (37·7° C); sulphuric acid, 144° Tw., use 1 gallon for souring.

These proportions are used in order to obtain the ordinary "Half Bleach," but, if a lighter colour should be required, the operations are repeated, using 80 gallons of the bleaching-powder solution without previous souring.

Second Method.—In this method, the bundles of yarn, weighing about 10 cwts., are treated in a series of tanks containing solutions of bleaching-powder of different strengths. Usually there are three tanks, the first containing 15 to 20 per cent. bleaching-powder (calculated on the weight of material); the second 10 to 15 per cent.; and the third 5 to 10 per cent.; the yarn is allowed to remain in each tank for from half to three-quarters of an hour at a temperature of 120° F. (48° to 49° C.) It is then washed and passed into the acid bath containing sulphuric acid at 1° Tw., where it remains half an hour; finally it is well washed and dried.

One great advantage obtained by this method is, that the yarn, which always appears very uneven after treatment in the first tank, need not remain so long in the strong solution of bleaching-powder as is necessarily the case with the first method, because the reaction is started in this solution and finished in the weaker ones. It is also interesting to note that, whenever tendering of the yarn does take place, it always occurs in the first tank, so that the time of treatment is regulated by the quality of the yarn, which also regulates the use of calcium hypochlorite or sodium hypochlorite; for with certain yarns better results are obtained with the calcium salt than with the sodium salt and *vice versa*. The treatment of the yarn during spinning has also some slight effect upon the bleaching operations, as it is necessary, whenever mineral oils have been used, to steep the yarn in hot water, and, in some rare cases, in a weak alkaline bath, previous to immersion in the bleaching-powder; but, with certain other oils, as, for instance, whale oil, this is not necessary. The most striking difference between the bleaching of jute and cotton is, that the jute is rarely, if ever, treated with alkali, the principal reason being that this occupies too much time, and is, therefore, too expensive; besides, the yarn loses too much in weight, while the final results are little better than that produced when the alkaline treatment is neglected. The total loss in weight which the yarn undergoes in bleaching varies from 6½ to 8 per cent.

For Jute Pieces, Cross & Bevan recommend the following process:—

1. The pieces are first treated with a solution of silicate of soda (4·8 kilos. silicate to 1,000 litres of water) at 70° C.
2. They are then passed through chloride of soda (sodium hypo-

chlorite) prepared from chloride of lime and sodium carbonate, and made of such a strength as to contain about 0·7 per cent., but not more than 1 per cent., available chlorine. The presence of soda completely prevents the formation of chlorinated products.

3. After being well rinsed, the pieces are passed through dilute hydrochloric acid ($\frac{1}{2}$ ° Tw.) to which a small amount of sulphurous acid has been added. The object of this treatment is to remove basic compounds which might subsequently, by the action of oxidising agents, bring about a discolouration of the fibre, and at the same time to dissolve away salts of iron. Wash and dry. The goods exhibit at this stage a light cream colour, possess a soft handle and a good lustre, and are ready to be dyed. But if intended for printing they must undergo the following process:—

4. Pass through a bath of bisulphite of soda containing from 1 to 2 per cent. of sulphurous acid, squeeze out the excess of liquid, allow to lie for 2 or 3 hours and dry on steam cylinders. By the drying, the sulphurous acid is driven off and the pieces leave the drying cylinders evenly impregnated with neutral sulphite of soda, which protects the fibre from the oxidising influences to which it is exposed in steaming, but does not prevent the development of the printed colours.

Properties of Bleached Jute.—Although it is generally supposed that during bleaching, the jute fibre suffers from the action of chlorine, this solely depends upon the quality of the yarn; since, with the better qualities, and by careful treatment, it is difficult to detect any deterioration whatever.

Chlorine does not act upon dry jute, even when the temperature is raised to 100° C., but in the presence of water, combines rapidly and with the evolution of heat. This chlorinated derivative is of a yellow colour and is soluble in alcohol, from which solution water precipitates a compound having the formula $C_{19}H_{18}Cl_4O_9$, as a yellow flocculent mass, which gives, when freshly precipitated, the characteristic magenta colouration with sodium sulphite.*

One remarkable feature of bleached jute, and one which may be looked upon as a disadvantage rather than otherwise, is the change which it undergoes when left exposed to the air; for, not only does it turn brown and darker in colour, but the fibre itself also seems to suffer, as it is slightly tendered, and becomes harsher and more brittle in quality. This change is effected more by temperature than by the presence of air; for, since on drying samples of the same bleached yarn in a vacuum for 7 and 14 hours respectively, and also, for comparison, in a water oven at 98° C., for the same time, very little difference between the one dried in the vacuum and the one dried in the air was noticed, although in both cases the colour had changed considerably; in fact, in the latter instance, the colour of the yarn was almost identical with that of the same yarn in the unbleached state. On

* *Journ. Chem. Soc. Trans.*, 1882, p. 98.

testing the strength of each, after the experiment, a slight tendering was noticed.

WASHING AND BLEACHING OF WOOL.

LOOSE WOOL.

As wool comes into the market, it usually represents a very impure article, containing from 30 to 80 per cent. of foreign substances. The impurities with which it is contaminated may be roughly classed under three headings, viz. :—

1. Fatty or wax-like bodies soluble in such solvents as bisulphide of carbon, benzene, or petroleum ether. This portion is generally known as the *yolk* or *wool-grease*.

2. Bodies soluble in water, consisting chiefly of the potassium salts of a number of organic acids. This portion is known as the *suint*.

3. Mechanically adhering impurities (earth, &c.) which adhere to, or are enveloped by, the suint and yolk.

Yolk or *wool-grease* consists principally of the higher solid alcohols, cholesterin and ischolesterin, in the free state and in combination with oleic and fatty acids, principally stearic and palmitic. These bodies, though difficult to saponify under ordinary circumstances, form emulsions with soap solutions, and can, therefore, be removed by soaping or by treatment with one of the solvents above named. To what extent exactly the wool-grease is removed by soaping or by treatment with solvents has not yet been definitely ascertained, but their effect appears to be restricted to the removal of those impurities only which envelop the fibre, and not of the grease contained in the interior of the fibre.*

The *suint* consists principally of the potassium salts of oleic, stearic, acetic, valeric, hyaenic, and other organic acids. It contains besides, nitrogenous substances, and small quantities of phosphates, chlorides, and sulphates.

The mechanically adhering impurities, lastly, consist chiefly of earthy matter, the composition of which varies with the nature of the soil on which the animals have been bred.

The removal of these impurities is absolutely necessary before the wool can be used for manufacturing. The operation of washing or *scouring* follows the operation of sorting; it is generally carried out by the manufacturer, but in rare cases by the dyer.

Formerly, wool was washed with stale urine (the active constituent of which is supposed to be ammonium carbonate), but this means, although still used in a few isolated cases on the Continent, may be said to have been almost entirely superseded in England by soap and soda. In Yorkshire, the largest centre of the woollen and worsted industries, the following simple process is almost invariably adopted. The wool is washed in three successive soap-baths, after which it is

* See *Journ. Soc. Dyers and Col.*, 1890, p. 18.

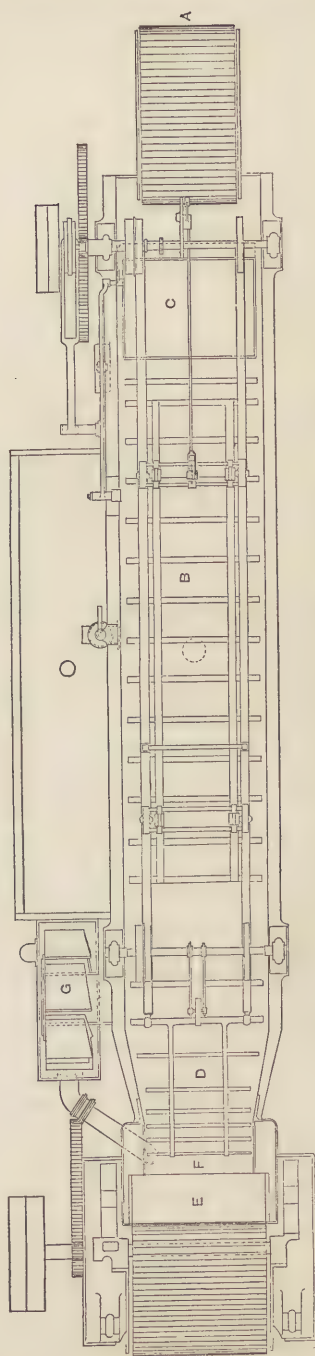
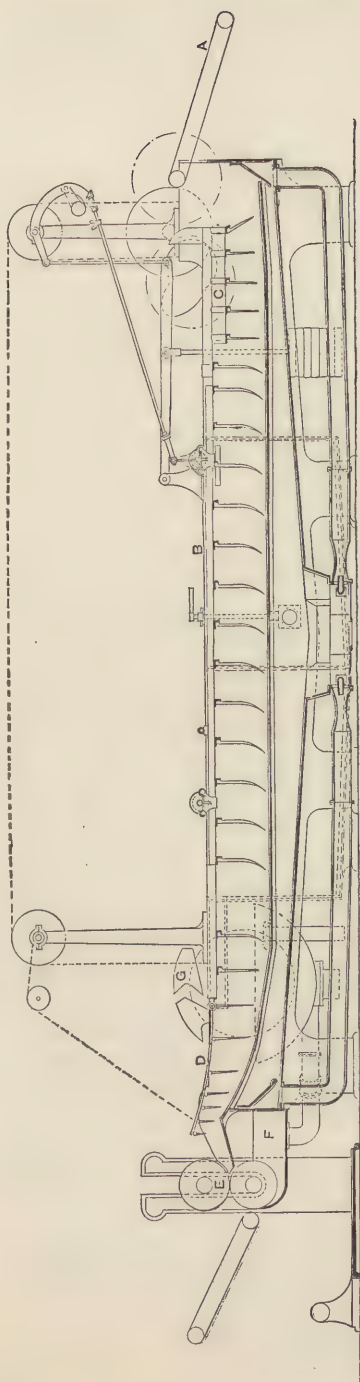
squeezed and dried in a current of air. The operations are seldom carried out by hand, but generally in specially constructed machines, described below.

For the finest qualities of wool, a soft soap prepared from Gallipoli oil is used. For the less fine qualities the soap is assisted in its action for cheapness' sake by additions of sodium carbonate or silicate. Cheaper qualities of soap are also frequently employed. The amounts of soap, or of soap and soda, necessary for washing vary considerably for the various qualities of wool, and are determined by practical experience. So-called pitchy wools, which contain a large amount of wool-grease, require most.

The temperature of the soap baths used in washing wool should, according to Dr Bowman, not exceed 35° C., if all the valuable properties of the fibre, more especially the lustre, are to be preserved. In working on the large scale this rule is, however, not often observed, considerably higher temperatures being employed.

Figs. 41 and 42 show in section and plan the construction of a wool-washing machine made by Messrs. T. & W. M'Naught, of Rochdale. It consists in the main of an iron tank (20 to 30 feet in length and about 3 feet broad, with a capacity of 650 to 1,300 gallons) provided with an automatic arrangement of forks or prongs, by which the wool is made to pass slowly through from the entrance to the delivery end. The raw wool is fed evenly on to the travelling apron, A, and is at once pressed, on entering the machine, beneath the surface of the suds by means of a perforated tray, C, called the immerser. Here it is seized by the prongs of the iron frame, B. The action of this frame is as follows:—It is lowered until the prongs are immersed in the suds, and whilst they are so immersed the frame makes a stroke forward. At the end of this the frame is lifted until the prongs are clear of the suds, when a backward stroke is made, and the prongs are again immersed and moved forward, and so on repeatedly. After a few strokes, a constant circulation towards the squeezing rollers is set up in the suds, the effect of which is to float the wool forward, almost without the assistance of the prongs, the point claimed being that it is scarcely touched in its passage through the tank save by the liquor. The delivering or lifting motion, D, consists of a light frame, with prongs hinged to the main frame, which is kept suspended by a chain. The points of the prongs follow the curved incline of the false bottom. The level of the suds is at the top of this incline, and the wool is partly floated and partly pushed over, after which it slips down fully charged with suds to the squeezing rollers, E. The liquor expelled here is caught by a small receptacle, F, below, and is lifted back into the tank again by a bucket wheel, G. The squeezing rollers are weighted, the pressure being given by a dead weight, which is conveyed through a spiral spring on the top levers.

Self-acting arrangements are provided for cleaning or flushing out the



Figs. 41 and 42. —Section and plan of M'Naught's wool-washing machine.

tank without removing the false bottom plates. By means of ejectors placed underneath the middle of the machine, a rapid circulation is given to the dirty water under the false bottom, when the tank has nearly run out, and thus the mud and dirt are carried off with the last portions of the water. If necessary, the bottom may then, in the same way, be washed over again with a little clean water.

A complete installation for wool washing consists of three machines.* The makers recommend for the first machine a capacity of 1,300 gallons; for the second and third, however, a capacity of only 650 gallons each. By adopting these dimensions, the tank of the first machine is capable of holding double the quantity of impurities in the space beneath the false bottom before a change of water is necessary, whilst the washing power is increased two-fold where it is most required. As the soap solution is discharged from the wool by the squeezing rollers at the end of the last machine, it is collected in a small receptacle, whence it overflows and passes through pipes to the side of the machine; the cleanest part of it is there lifted by revolving buckets into the tank, and the remainder run on to the second machine, precisely the same action taking place between the second and first machines. But the discharge water from the squeezing rollers of the first machine is allowed to run away to the main drain, or to be collected so as to extract the grease from it, which is usually done by large firms. The dirty water which eventually passes away from the machines in the manner described, is replaced from an auxiliary tank, containing a quantity of clean water already charged with the necessary amount of soap, and heated to the proper temperature ready for use.

The drying of loose wool after washing may be done in the open air, but this process is seldom resorted to in England owing to the space required and the uncertainty of the weather. A simple contrivance largely adopted by wool washers consists of a flat table covered with galvanized wire netting, through which a current of heated air is sent from below by means of fans. The wool is spread evenly on the netting, and is thus dried in a short time.

Machines are also constructed by various makers, in which the drying of the wool is effected continuously, being passed along aprons or endless bands through a chamber in which it meets a current of hot air.

In M'Naught's continuous wool-drying machine† the drying is effected by passing the wool as it leaves the squeezing rollers of the last washing machine into a large revolving perforated cylinder, working at an incline of about $\frac{3}{4}$ in. to the foot. The smallest size

* The third or last tank contains a solution of pure soap only. To the solution in the first machine a further addition of soap and usually sodium or potassium carbonate is made. It has been recommended to use water only in the last machine, but in practice this has not been found to give satisfactory results.

† See *Text. Man.*, June, 1890.

made is 20 ft. long by 8 ft. diameter. As the cylinder revolves, the wool falls gradually towards the delivery end, and is dried in its passage through the cylinder by warm air admitted through the perforated sides.

BYE-PRODUCTS OBTAINED IN WOOL WASHING.

Some wools which come into the market have already been deprived of a portion of their impurities by a simple washing in water, either on the sheep's back or after shearing.* The resulting wash-waters are generally allowed to flow away, but by proper manipulation, they may be worked up for a valuable bye-product—potassium carbonate—in places where fuel is cheap. The same bye-product may be obtained from all wools which come into the hands of the manufacturer in the raw state; but, although this has been done for years on the Continent, little use has hitherto been made of the fact in England. The chief reason of this appears to be that in washing first with water alone, a considerable quantity of fatty matter is lost, which would otherwise be regenerated. Nevertheless, the value of the potassium carbonate appears to exceed that of the lost fatty matters, and in consequence of this, several establishments in England have of late years begun to manufacture the former article as a bye-product.

In order to work economically as regards fuel, it is necessary to adopt the counter-current system in extracting the wool. For this purpose, a simple contrivance consisting of a series of five or six communicating vats may serve. The vats are placed on an inclined plane, so that the water from the top one may flow by its own gravitation to the second, from the second to the third, and so on to the bottom. The raw wool is placed in iron or wicker-work baskets, first in the bottom vat. After it has remained there for a short time, the baskets are transferred to the next vat higher up, a fresh lot being put into the bottom vat; and so on, until the first lot which was put in has reached the top vat, where it comes in contact with the clean water. By means of a system of this kind, a much more complete and rational extraction can be effected than by using only one water.

Cold water may be used for extracting, but the results are much better if the water is first heated to about 45° C.

The strong, dirty, brown liquor thus obtained is evaporated down to dryness and calcined in specially constructed furnaces, for details of which reference may be made to works dealing with the manufacture of alkali.

The amount of potassium carbonate thus obtained, calculated on the weight of the wool employed, varies from 1 to 8 per cent., and is, on an average, about $3\frac{1}{2}$ per cent.

Wool-grease.—In most small works, the waste water obtained from wool washing is allowed to run away; but in the better regulated

* Colonial wools are sometimes washed in this way in order to save carriage.

and large establishments, this waste water is specially treated for the purpose, not only of getting from it the fat contained in the wool, but also of regenerating the fatty matters from the soap used in washing.

For this purpose, the waste water, which consists essentially of an emulsion of the wool-grease in soap solution, is first allowed to settle in large tanks, in order that the coarser solid impurities may sink to the bottom. An excess of crude sulphuric acid is then added, which decomposes or "breaks," the soap and the fatty acids rise to the surface, bringing with them the whole of the wool-grease in the form of a dirty-looking magma. After the greater part of the water has been got rid of by allowing the magma to strain in canvas filters, the latter is packed in sheets of canvas and hot-pressed. The liquid wool-grease is then heated in metal vessels until the greater part of the solid impurities has settled, when it is run into casks where it solidifies. In some works the cake from the process is extracted with bisulphide of carbon, in order to obtain the last portions of the wool-grease which mechanically adhere to it. Wool-grease or "Yorkshire grease" is used as a lubricant, and for smearing sheep in winter in cold climates, while a large proportion of what is produced is distilled for the manufacture of stearin and olein. Many attempts have been made to utilise it for the manufacture of soap, but although this is not impossible, the expense is prohibitive.

Another method* of regenerating the wool-grease is to precipitate with calcium chloride, which throws down the soap as an insoluble lime-soap and along with it the wool-grease. The magma is then treated with hydrochloric acid for the purpose of decomposing the lime-soap and removing the lime. The further treatment is the same as in the first method.

A pure form of wool-grease is sometimes obtained from the waste wash water by passing the clarified liquor through centrifugal machines running at a very high speed, such as are used in creaming milk. By again emulsifying the grease thus obtained, and passing it for a second time through the centrifugal machine, a creamy white substance is obtained, to which the name of *Lanolin* has been given, and which finds a limited application in pharmacy for making up salves, &c.

Wool Washing with Volatile Liquids.—Numerous endeavours have been made from time to time to dispense altogether with the use of soap in the washing of wool, the objects being to cheapen the operation and to obviate the injurious effects of the hot or warm soap solution which causes to a certain extent a felting and diminution in the lustre of the fibre. An account of the various machines which have been patented with this object will be found in a paper by J. J. Hummel in the *Journal of the Society of Dyers and Colourists*, 1890, p. 2.

* See *Journ. Soc. Dyerz and Col.*, 1888, p. 197.

The machines devised for the purpose differ greatly from each other in their construction, but the principle is similar in nearly all the systems proposed—viz., treatment of the wool in a volatile solvent, such as bisulphide of carbon, benzene, toluene, petroleum-ether, &c.—for the purpose of removing all the wool-grease; and then in water for the purpose of removing the suint, or *vice versâ*. Several processes based upon this principle, which should theoretically give the best results, not only with regard to the washing, but also to the complete recovery of the bye-products, have been tried and found to answer well on the small scale. But on the large scale practical difficulties have always shown themselves, in consequence of which none of the methods has hitherto been able to hold its own against the old process of washing with soap. Within the last few years, two processes—viz., those of Singer & Judell and of Burnell—have come into prominence, and have been tried on the large scale. The principle adopted in Singer & Judell's system is to pass the wool, which is carried between two endless bands of brass netting, first through a series of vats containing bisulphide of carbon. The excess of liquid is squeezed out of the wool as it leaves each vat, by means of a pair of rollers. The endless band containing the wool then passes in a similar manner through a series of water tanks, in which the suint and the mechanically adhering bisulphide of carbon are removed. The whole machine is covered by a hood, which is hermetically sealed by water seals at all points except where the endless band enters and passes out again, and a small opening at the top by means of which a gentle current of air is maintained through the apparatus.

Both in the bisulphide and in the water tanks, the counter-current system is adopted; so that the regeneration of the pure wool-grease and of the potash are mere matters of detail. The saturated bisulphide flows from the last tank into a specially constructed retort, from which the molten wool-grease is obtained in a continuous stream, while the fresh distilled bisulphide is passed again into the first tank. For a full description of the machine, see a paper by Watson Smith on "Wool and fur, modes of cleansing them, &c."* A machine of this kind was erected at the extensive wool-combing works of Messrs. Isaac Holden & Sons in Bradford, where it appears to have worked successfully for a short time. But the occurrence of an explosion in the machine, which destroyed part of it, caused the proprietors to give it up.

Burnell's machine consists of two wrought-iron vessels, in the first and larger of which the wool is caused to pass slowly through petroleum spirit, being pressed in its passage through the liquid by means of a series of about 20 rollers against a large central cast-iron bowl or drum. In the second vessel the wool is similarly treated in warm water. The counter-current system is also adopted in this machine, and the bye-products may be recovered as in the foregoing system.

* *Journ. Soc. Dyers and Col.*, 1889, p. 19.

WOOLLEN AND WORSTED YARN.

As they are delivered to the dyer, most woollen and worsted yarns contain oil which is purposely added in order to facilitate the spinning. Worsted yarns contain, on an average, about 2 to 6 per cent. of olive oil, while the amount of oil put into shoddy yarn may in some cases exceed 15 per cent. of the weight of the material. Worsted yarns spun on the French system (mule-spun) contain no oil.

It is necessary to scour the yarn before dyeing or stoving for the

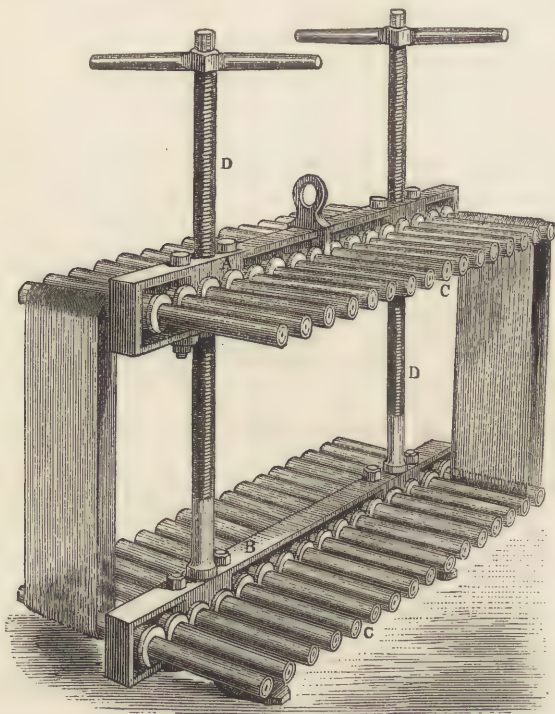


Fig. 42a.—Stretching frame for worsted yarns.

purpose of removing the oil. If this is omitted, the presence of the oil will cause the yarn to wet out badly and unevenly, and uneven dyeing will result. For cheap blacks the scouring is sometimes omitted.

Some yarns, especially those made from lustre wool, have the property of "curling" when brought in contact with water to such an extent that the whole hank might become entangled. In order to avoid this, such yarns are "stretched" before scouring. For this purpose, the hanks are tightly stretched on a frame like that shown in the figure, which, when filled, is immersed in boiling water for about

half an hour, then again taken out and allowed to cool. The position of the hanks on the spindles is then changed by turning them half round, and the frame is again immersed in the boiling water for some minutes. The yarn thus becomes evenly stretched, and is found to have completely lost its property of curling. By means of an improved arrangement, patented by Frusher, a second stretching is rendered unnecessary, the spindles or arms of the stretching frame being caused to revolve slowly.

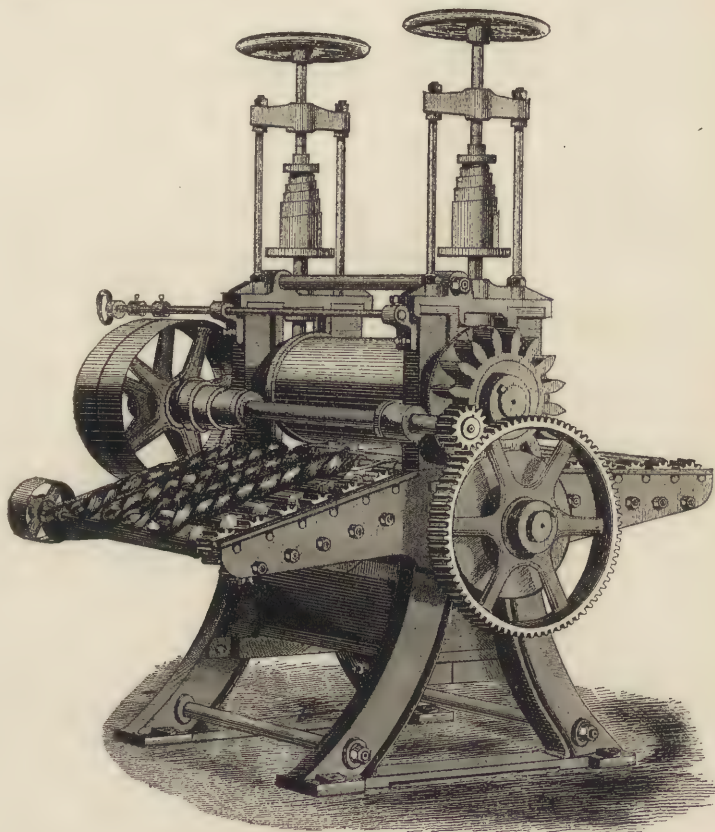


Fig. 43.—Squeezing rollers for woollen or worsted yarns (*Haubold*).

The scouring is done with a solution of soap, or of soap and soda, at a temperature of 35° to 45° C. In some works the operation is conducted in rectangular wooden vessels, heated by steam, capable of holding on an average 100 lbs. of yarn. The hanks are suspended in the soap solution on sticks which lie across the vat. The hanks are turned two or three times, after which they are taken out and washed in water to remove the surplus soap solution. They are then hydro-extracted, and are ready to be dyed.

A simpler and more rapid method consists in turning the hanks two or three times by hand in the soap solution which is contained in a square wooden vat, at the side of which there is a pair of squeezing rollers with a travelling apron leading up to them. Fig. 43 shows a pair of squeezing rollers specially constructed for this purpose. The rollers are of cast iron, and are covered with some soft protecting material (such as silk noils) to prevent the yarn being damaged. The pressure is produced by springs, and can be regulated by the screws shown at the top. In this machine, the travelling apron is replaced by a number of wooden rollers.

In working by this method, the operator always has two hanks in the liquid, one of which he turns while the other is allowed to soak.

The one which he has turned two or three times he throws into the travelling apron, by which it is carried to the squeezers. Before beginning to turn the second hank he puts a fresh one in to soak, and so on. After scouring, the hanks are washed and hydroextracted, as above.

Although several machines have been devised for washing woollen and worsted yarns, they have met with little favour among dyers. One arrangement of this kind consists of a rectangular

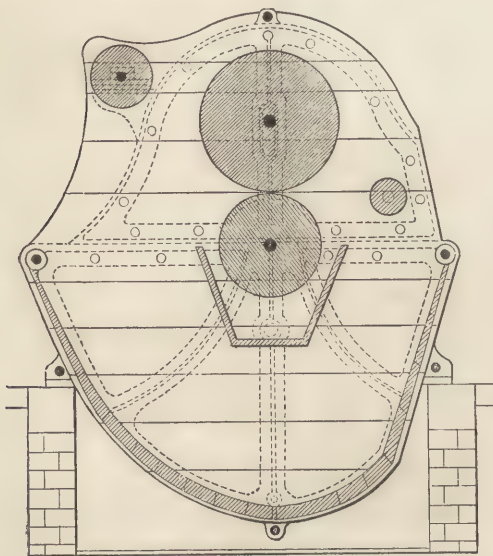


Fig. 44.—Washing machine (dolly) for woollen pieces.

wooden vat containing the soap solution. At one end there is a travelling apron and a pair of squeezing rollers, while over the vat are three bobbins which have an alternate backward and forward motion. The yarn is suspended on the bobbins, and the turning, otherwise done by hand, is done by the machine. There does not, however, appear to be any saving in labour since some one must be there to put on and take off the hanks from the bobbins. It is questionable whether such a machine offers any advantages over the method of washing by hand.

In dealing with large quantities, the hanks are sometimes tied loosely together, end to end, with string, and passed in rope-form two or three times up and down through the soap solution, and then through a pair of squeezing rollers covered with some soft material.

The *waste waters* from the washing of woollen and worsted yarns consist essentially of an emulsion of oil in soap; and should not be allowed to flow away, since the regeneration of the soap does not present any difficulties. It suffices to run the waste waters into tanks, add an excess of sulphuric acid, and collect, drain, and hot-press the resulting magma of fatty acids and oil. The resulting grease can easily be converted into soap by boiling with the necessary amount of caustic alkali or of a mixture of carbonate and caustic.

WOOLLEN AND WORSTED PIECES.

In the manufacture of plain goods it is not usual to scour the yarn

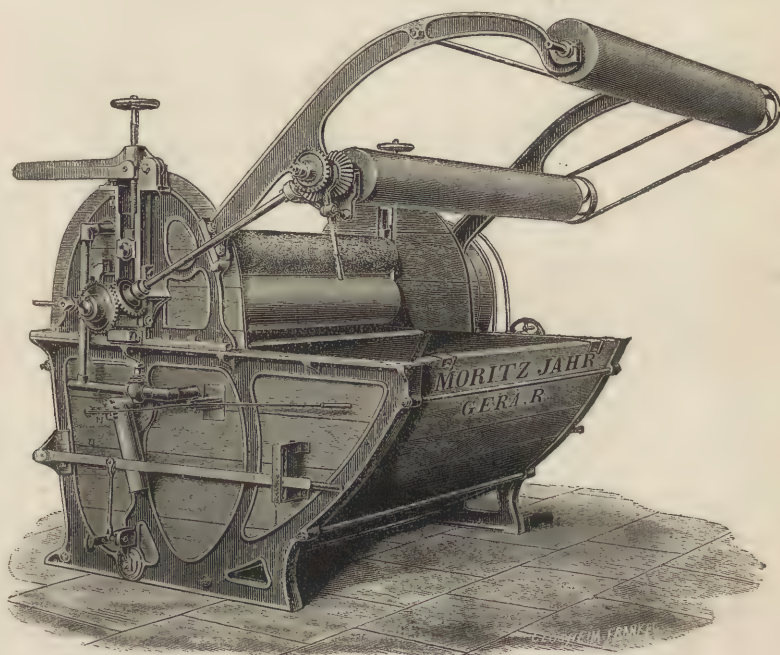


Fig. 45.—Broad-washing machine.

before washing; such pieces, therefore, contain all the oil which was originally contained in the warp and weft. For common blacks or heavy woollens, the oil is frequently left in, the pieces being mordanted and dyed without scouring previously. Low class worsted coatings are simply washed in soda and then steamed. But for better class blacks and for colours, all piece goods are first scoured in soap or in soap and soda.

Generally this is effected in a washing machine known as a “dolly” (see Fig. 44), in which the pieces (sewn together into an endless band) are made to pass through the scouring liquid contained in

the large outer vessel and between two wooden bowls. The upper heavy bowl rests with its own weight on the pieces and serves to draw the pieces through the liquid, at the same time expressing

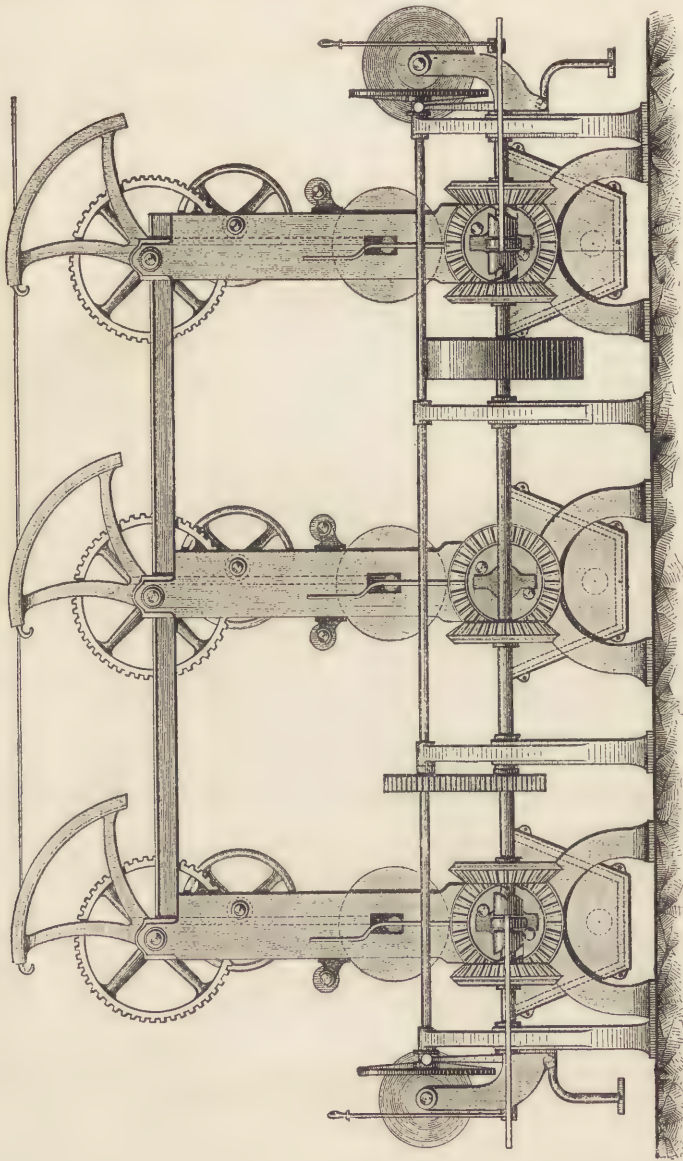


Fig. 46. — Treble crabbing machine,

the dirty wash water from them, which collects in the trough below the lower bowl and flows away. For pieces which are liable to crimp or crease the dolly is not suitable. Such goods are washed

in broad-washing machines, one of which is shown in Fig. 45. In principle these machines are similar to the dolly, the only essential difference being that the pieces are made to pass through

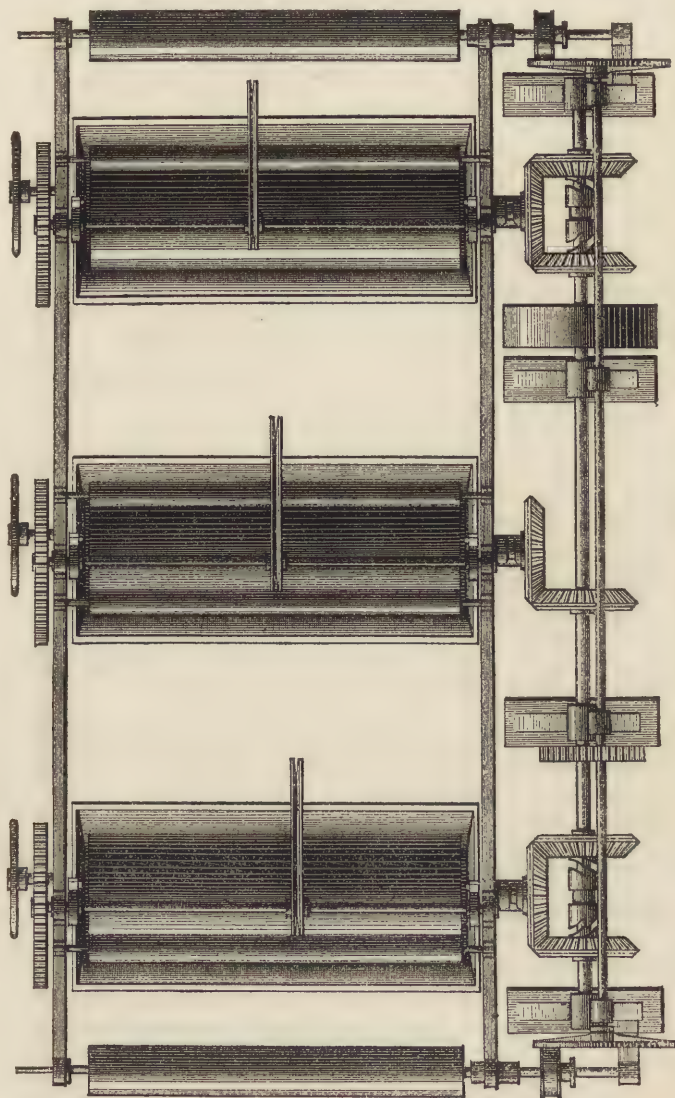


Fig. 47.—Treble crabbing machine.

the rollers and the scouring liquid at full breadth instead of in rope-form.

After scouring, the goods are washed in water to remove the soap.

MIXED GOODS.

Pieces made with cotton warp and worsted weft "cockle" when put into water—*i.e.*, the surface of the piece becomes uneven owing to the different degree of contraction of the two fibres. By stretching, or dyeing in a stretched state, this unevenness can be overcome, but it will show itself again as soon as the material gets wet. The same defect shows itself, though in a more limited degree, in worsted fabrics in which the warp and weft are made of different classes of wool.

Crabbing.—Such goods are subjected before scouring and dyeing to an operation termed "crabbing," which is analogous to the stretching of worsted yarn, and which causes the setting of the piece in such a manner that it does not cockle when wetted. In crabbing, the pieces are drawn at full breadth and under considerable tension through boiling water, beamed and allowed to cool. They then retain the stretched position in which they were beamed, provided that they are not subsequently subjected to a higher temperature than that of the water through which they were drawn.

Figs. 46 and 47 show a treble crabbing machine with iron rollers, in which the pieces can be drawn twice in succession through the boiling water and beamed. The third bowl contains cold water. Of each pair of rollers, the lower one is driven by spur gearing, while the upper one can be raised or lowered at will for the purpose of decreasing or increasing the pressure.

Both tension and pressure are regulated by experience to suit the finish subsequently required.

In order to expose the pieces in the stretched condition to a higher temperature than they will be exposed to during any of the subsequent operations of dyeing and finishing, they are steamed. The last roller on which they are beamed is a perforated iron cylinder. The outside of the pieces on the cylinder is enveloped in canvas, and steam at about 40 lbs. pressure is admitted through the bottom axis, until it has traversed the whole thickness of the layer of material. After the first steaming, the pieces are allowed to cool, and are drawn under tension on to another perforated cylinder and steamed again. In this manner, those portions of the piece which were furthest away from the centre (where the temperature is greatest) come nearest the centre, and the effect of the steaming is more even. If this second steaming is omitted, the goods may become "ended," a fault which is due to the fact that high-pressure steam imparts to the wool an increased affinity for colouring matters. But, although twice steaming equalises to a certain extent the effect of the steaming in this respect, those pieces which lie in the middle are necessarily exposed to a less severe action than the ends. It should be borne in mind that wool is easily affected by steam at high temperatures, and that too high a pressure in steaming may easily result in a tendering of the material.

The position of the cylinders in steaming may either be vertical or horizontal, but in both systems unevenness may result from condensation. This danger may be avoided in horizontal cylinders by causing them to revolve slowly during the steaming. An arrangement of this kind in which the steam may be caused to pass through from the centre or towards the centre has been patented by Clay (Engl. Pat., No. 19,377, 1889).*

Fig. 48 is a longitudinal section of the machine, which comprises a box or chest, A, provided with a lid or cover, B, capable of opening upon hinges. As it is necessary for the box or chest to be steam- or air-tight, the lid, B, is hermetically sealed to the lower part of the chest by screws and nuts. The cloth or fabric to be treated is wound upon a perforated cylinder, M; the journal, N, of the cylinder is made hollow and is inserted into the tubular revolving shaft, O. The

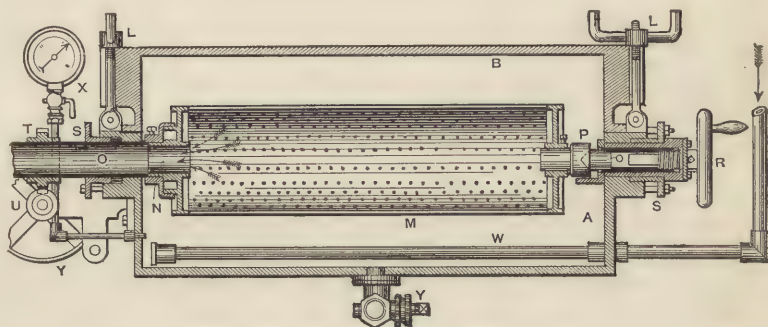


Fig. 48.—Clay's steaming arrangement.

opposite end of the perforated cylinder is closed and provided with a cup, P, for receiving the centre, Q, which is made to move endwise to and from the cup by the hand wheel, R, after the manner of the spindle in a slide lathe. Each end of the box or chest is provided with stuffing boxes, S, which permit of the parts revolving whilst remaining steam-tight. The hollow revolving shaft, O, causes the perforated cylinder to revolve, the hollow shaft receiving its rotary motion by means of a worm wheel, T, gearing with a worm, U, driven by the driving pulleys, Y.

The *modus operandi* is as follows:—The hollow shaft, O, is placed in communication with a pump or exhaust fan, the result being that the air is drawn through the fabric, and through the perforated cylinder, passing away through the hollow shaft. When a vacuum has been thus formed, steam is introduced into the box through perforated pipes, W, and is drawn through the fabric by the exhausting fan or pump. The pressure of the steam within the chest is indicated on the steam gauge, X. The perforated cylinder continues to revolve during the steaming action, and the length of time the steaming is continued will

* *Journ. Soc. Dyers and Col.*, 1891, p. 159.

depend upon the class of goods under operation, and the discretion and judgment of the operator. Y represents a valve for emptying the chest or box. Provision may be made for collecting the ejected liquid in any suitable form of receptacle, so that it may be re-used.

By a suitable arrangement of valves attached to the pump or fan, steam can be forced through the fabric in the reverse manner to that described, whereby both the inner and outer surfaces of the rolled fabric will be equally acted upon. Liquids may also be applied to the fabric in the same manner, and by connecting the valve, Y, to the pump or fan a complete circulation of the dye or other liquor is obtained.

After crabbing and steaming, the pieces are scoured previous to dyeing. The scouring is sometimes effected with advantage in the crabbing machine by substituting for the water in the first bowl a solution of soap or soda, or a mixture of both. This prevents the "setting" of the grease in the wool. When once "set" the grease is difficult to remove. No investigations appear to have been made for the purpose of investigating the cause of this fault.

BLEACHING OF WOOL.

The method usually adopted for the bleaching of wool differs entirely from those used for the vegetable fibres. Indeed, were wool to be subjected to the same treatment as cotton, it would be completely dissolved in the first lime-boil. Nor has a treatment with chloride of lime any beneficial effect in removing the natural yellow colouring matter of the fibre.

The bleaching agent most usually employed is sulphurous acid, either gaseous or in solution, but generally gaseous. The operation is technically known as *stoving*.

For the stoving of worsted or woollen yarns, the hanks, after having been carefully scoured, are blued in a weak soap bath containing a slight quantity of some such colouring matter as indigo carmine, methyl violet, methylene blue, &c., and are then hydro-extracted. They are then suspended on wooden rods and placed in the sulphur stoves, where they are exposed for 6 to 8 hours, or over night, to an atmosphere of sulphurous acid produced by simply burning stick sulphur in the stove in an iron pot. The usual sulphur stove consists of a small brick or stone chamber, 5 to 6 ft. broad, 8 to 10 ft. deep, and about 6 ft. high, lined with wood or glass. Care is taken in constructing such stoves to exclude all iron or other metals (wooden pegs being used in place of nails, &c.), since they would soon be destroyed by the acid atmosphere and might give rise to stains on the yarn. The average quantity of sulphur used is 6 to 7 lbs. for every 100 lbs. of wool.

When the operation is over, the doors of the stoves are opened, a draft of air is drawn through by removing the lid of an opening at the bottom end of the stove which is in connection with the works' chimney, and the yarn is taken out, aired, and dried.

For pieces the process is the same, but the construction of the stove is different. The pieces are sewn together, end to end, and pass through a narrow slit in the side of the stove, then many times up and down over wooden rollers, and ultimately out again at the same slit.

The bleaching action of the sulphurous acid is quite different to that of chlorine. Some regard it as a reduction of the yellow colouring matter of the wool to a colourless leuco-compound, analogous to the reduction of magenta to colourless leuco-rosaniline by passing sulphurous acid into the solution. By others it is supposed that the sulphurous acid combines chemically with the colouring matter, forming a colourless and soluble sulphurous acid compound, analogous to alizarin blue S or coerulein S (*q.v.*). That the change is not a permanent one is shown by the fact that stoved wool, if treated with alkalies like soap or soda, again assumes its original yellow tinge.

Stoved wool tenaciously retains the sulphurous acid with which it has been treated. In stoved yarns, which are subsequently woven into coloured fancy fabrics, this fact is frequently a drawback, since the sulphurous acid in the stoved yarn may frequently bleach coloured yarns which cross it. In order to avoid this, Lunge recommends a treatment of the stoved yarn with peroxide of hydrogen by passing it through a dilute solution of this reagent. The sulphurous acid is thus rapidly and completely converted into sulphuric acid (which is harmless), while at the same time a further bleaching takes place.

In place of stoving, wool may be bleached by means of a solution of sulphurous acid or bisulphite of soda. In bleaching with sulphurous acid, the wool, previously well scoured, is steeped for 24 hours in a strong solution of sulphurous acid, wrung, and washed. For preparing the sulphurous acid solution, the liquefied sulphur dioxide, brought into the market by Messrs. Boake & Co. in copper drums, is a convenient article. Free sulphurous acid has the disadvantage of injuring the health of the workpeople.

For bleaching with bisulphite of soda, Justinus Mullerus recommends the following process:—The scoured wool is steeped for 12 to 15 hours in a solution of bisulphite of soda at 32° Tw., and after wringing, but without washing, it is passed through sulphuric acid at 6° Tw. Sulphurous acid is thus generated on and in the fibre.

Bleaching of Wool with Hyposulphite of Soda.—The bleaching agent first proposed for this purpose by Kallab* is prepared by gradually adding zinc powder to commercial bisulphite of soda diluted with about four times its bulk of water until no further reaction takes

* See also Dommergue, *Journ. Soc. Dyers and Col.*, 1890, p. 111.

place. Milk of lime is then added in order to precipitate the zinc; and the clear supernatant liquid, which marks $1\frac{1}{2}^{\circ}$ to 5° Tw., is used for bleaching. Small quantities of acetic acid and of finely-ground indigo are added to the bath. The latter serves for blueing, but it is not clear what is attained by the addition of the acetic acid. The wool to be bleached is scoured and then immersed in the bleaching liquor for 12 to 24 hours. It is then taken out, washed in weak soda solution, then in water and exposed to the air, when the reduced indigo is oxidised on the fibre.

Bleaching of Wool with Hydrogen Peroxide.—This method at present only finds a limited application on wool owing to the expense of the bleaching agent. Ebell* recommends the following process:—The wool is immersed in hydrogen peroxide of 3 per cent., to each litre (100 galls.) of which are added 20 cc. (2 galls.) ammonia (sp. gr. 0.910) and left at the ordinary temperature (12° to 17° C.) for 24 hours. If the temperature is raised to 30° C. the bleaching proceeds more rapidly and is finished in 8 to 10 hours. Another method suggested is to steep the wool in the ammoniacal solution of hydrogen peroxide, wring it evenly, and dry in the air at the ordinary temperature. During the drying, the peroxide becomes concentrated on the fibre (according to Ebell) from a strength of 3 to 20 per cent., before an appreciable decomposition begins to take place, and it thus acts much more energetically.

The bleaching effect of hydrogen peroxide is undoubtedly due to oxidation; but our knowledge of the reaction ends here, since we are unacquainted with the nature of the substances which it removes.

Peroxide of hydrogen is also used largely for the bleaching of *feathers*.

Bleaching of Woollen Pieces for Printing.—A common practice is to pass the pieces, after stoving, through chloride of lime acidulated with hydrochloric acid. This treatment destroys all the sulphurous acid retained by the fibre and chlorinates the wool, thus imparting to it a greater affinity for colouring matters.

H. Koechlin recommends the following process:—The pieces are drawn at full breadth through hydrogen peroxide of 12 volumes diluted with 2 to 10 times its volume of water, according to the thickness of the material, the stronger bath being required for the denser textures. They are then squeezed, beamed on wooden rollers, and allowed to lie for 24 hours in this state. Then follows a treatment in bisulphite of soda at 64° Tw., also diluted with 2 to 10 parts of water. The pieces are beamed again and dried. They are then washed and chlorinated in a dolly with about 6 per cent. chloride of lime and excess of hydrochloric acid. After chlorinating they are washed and dried; and are then ready for printing.

* *Journ. Soc. Dyers and Col.*, 1888, p. 29.

DISCHARGING AND BLEACHING OF SILK.

Raw silk generally has a coarse appearance and a harsh feel; and is, consequently, seldom made use of for manufacturing purposes. In order to bring out its characteristic and valuable properties, it is necessary to remove the silk gum or sericine, which gums the individual fibres together. The operation which is known as un-gumming, stripping or discharging may be effected in various ways, of which the following is the one most generally adopted. The operation is carried out in two stages.

1. Boiling-off.—The hanks of silk suspended on wooden sticks are immersed in a soap solution contained in a rectangular wooden vat, the sides of which are covered with canvas. The soap usually employed for this purpose is a good neutral Marseilles or olein soap, and the amount taken varies from 30 to 35 per cent. of the weight of the silk. The temperature of the bath should be 90° to 95° C.; boiling must be avoided, since it would tend to entangle the silk and would cause the yellow colouring matter which is contained in some silks to become fixed on the fibre. The hanks are turned from time to time in the hot soap solution for 1 to 1½ hours, during which the silk at first swells up considerably and becomes sticky; but, as the sericine is dissolved off, the individual fibres begin to make their appearance and the silk becomes soft and glossy. For white silk or delicate colours, the boiling-off is not done in one, but in three, separate baths, in each of which the hanks are turned for 20 to 30 minutes. As soon as the first bath has become charged with silk gum, it is emptied and filled with fresh soap solution and then serves as the last bath, and so on; so that a sort of counter-current is established, in which the fresh hanks are always treated with the soap solution which has been used twice over, while the last treatment is effected with fresh soap solution.

The thick waste liquor which comes from the last bath is a solution of sericine in soap, and is used as an addition to the dye-bath in dyeing silk with coal-tar colours, under the name of *boiled-off liquor*.

Soft water only should be used for boiling off, calcareous impurities being liable to mar the lustre of the silk. If none but hard water be available, it must be previously softened or corrected by suitable treatment, which will depend upon the nature of the hardness.

Some silks contain a small amount of lime in the sericine. To remove this, the hanks are steeped, before boiling-off, for a short time in dilute hydrochloric acid, after which they are washed and passed through a weak solution of soda crystals.

The boiled-off silk is rinsed in weak soda solution and wrung. At this stage it can be dyed in dark colours, but if it is to be dyed white or in light colours, it is subjected to the next operation.

2. Discharging.—The boiled-off hanks are tied loosely together with smooth tape, placed in coarse linen bags and boiled in round copper boilers for $\frac{1}{2}$ to 3 hours, according to the quality of the silk, with 10 to 15 per cent. Marseilles soap. The hanks are then taken out, rinsed in weak soda solution, then in running water, wrung out evenly and dried. The old soap solution is preserved and used again in boiling-off.

The average loss in weight experienced in the boiling-off and discharging amounts to 25 to 30 per cent. for European, 18 to 22 per cent. for Japanese and Chinese silks.

Silk being an expensive article, such losses in weight materially affect the price of the finished article, and the dyer is frequently desired to reduce the loss to a minimum by means of a different mode of treatment.

Souple Silk is raw silk which has been treated in such a manner as to make it fit for dyeing, while the sericine is only partially removed. The process, as carried out in Lyons and St. Etienne, embraces, according to Wagner-Fischer,* the following operations:—

1. *Scouring (dégraissage).*—The silk is turned for 1 to 2 hours in a solution containing 10 per cent. of soap at a temperature of 25° to 35° C. This treatment effects the removal of the fatty and wax-like impurities, and at the same time softens the fibre and causes it to swell. The operation is repeated.

2. *Bleaching (blanchiment).*—The scoured silk is turned for a quarter of an hour in a solution of aqua regia † at 3° to 4° Tw. Too long an immersion in the acid must be avoided, otherwise the silk is liable to be turned yellow by the nitric acid. In place of aqua regia, many dyers prefer a solution of “nitrose” (solution of nitrous acid in concentrated sulphuric acid) in water.

As soon as the silk has assumed a greenish-grey colour, it is taken out and washed well in water.

Stoving (soufrage).—The hanks are well and evenly wrung out and exposed in sulphur stoves (see *Woollen Bleaching*) for 6 to 8 hours to an atmosphere of sulphurous acid. The operation is repeated several times according to the degree of white required.

Soupling (assouplissage).—The object of this operation is to soften the silk which has become hard and brittle by the foregoing operations. It is softened by turning the hanks for about 1½ hours in a solution of 3 to 4 grms. tartar per litre and washing, after this treatment, in warm water. In place of tartar, magnesium sulphate may be employed.

Souple silk is not as strong as boiled-off silk, and is only used for

* *Chem. Techn.*

† The aqua regia is prepared by mixing 5 parts hydrochloric acid of 32½° Tw. with 1 part nitric acid at 61¼° Tw.; and allowing the mixture to stand for 4 to 5 days at 28° C. It is then diluted down with water to the required strength.

weft. The loss in weight averages 6 to 8 per cent. It may be dyed in acid baths without any special precautions, but if dyed in soap baths the temperature should not exceed 50° to 60° C.; otherwise the appearance of the silk suffers and a loss in weight results. For blacks the operations of bleaching and stoving are omitted.

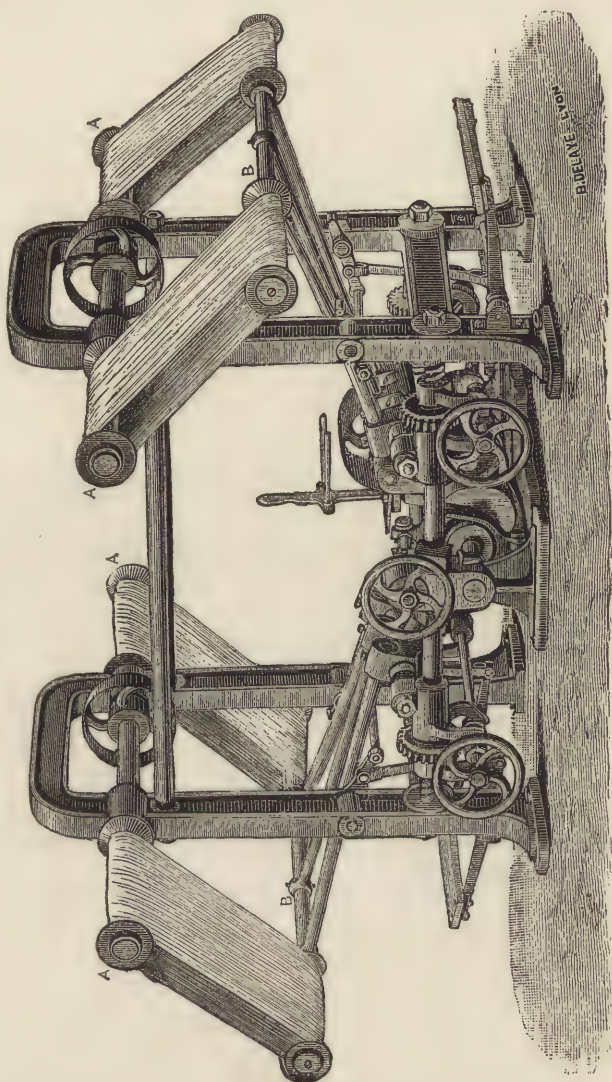


Fig. 49. — Corron's stretching machine.

Ecreu Silk is raw silk which has been scoured in a weak soap solution to remove fatty and wax-like impurities, and then bleached by stoving. For blacks the stoving is omitted. The loss in weight amounts to 1 to 4 per cent. Ecreu silk has a harsh feel, and is used for warp.

Silk is frequently discharged in the piece. This is especially the case with satins (silk warp and cotton weft). The *modus operandi* is similar to that described for yarn. The object of discharging such goods in the piece is to facilitate the weaving. Weighted coloured satins are often produced by first treating with some tannin matter (*e.g.*, sumach), then steeping in a concentrated solution of stannic chloride, washing off, and then boiling off in the piece. In this manner the silk is weighted, while, at the same time, the cotton is mordanted for basic aniline colours.

In order to bring out to the fullest possible extent the characteristic and valuable properties of the fibre, the discharged silk is subjected in the hank to the following mechanical operations:—

1. **Stretching** (*sécouage*).—This operation may take place before

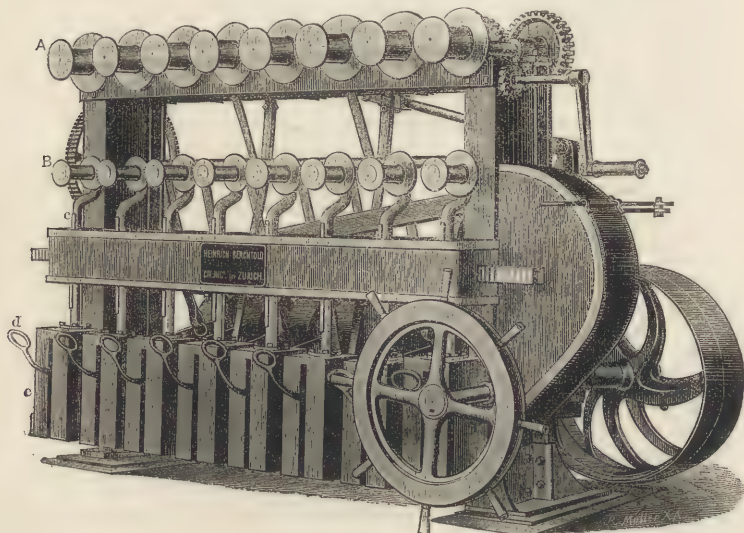


Fig. 50.—Silk glossing machine.

or after dyeing. The hanks are suspended on a stout, smooth, wooden peg, one end of which is fixed in the wall. By means of a smooth stick placed inside the hank, the operator stretches it by repeated jerks, the hank being turned on the peg from time to time. In this manner silk which has not been completely discharged may be stretched without disadvantage 2 to 3 per cent. in length. In order to save hand labour, the machine of C. Corron (Fig. 49) may be used for this purpose. The construction of the machine aims at an automatic imitation of the operation as carried out by hands. Four hanks are treated simultaneously, being suspended on the slowly rotating bobbins, A, while the stretching is effected by the intermittent raising and falling of the bars, B.

Stretching is used largely for spun silk.

2. Glossing (*chevillage*).—The object of this operation is to increase the gloss of the fibre. This is sometimes done by hand by twisting the hanks very tight and allowing them to remain so for several hours. The operation is frequently repeated.

But, for this purpose, hand labour has been almost entirely superseded by machinery. Fig. 50 shows a silk glossing machine (H. Berchtold, Zürich). The hanks are suspended on the bobbins, A. The bobbins, B, are inserted in the hanks and stretch the yarn by means of the heavy weights, *e*, being on their extremities. By an automatic

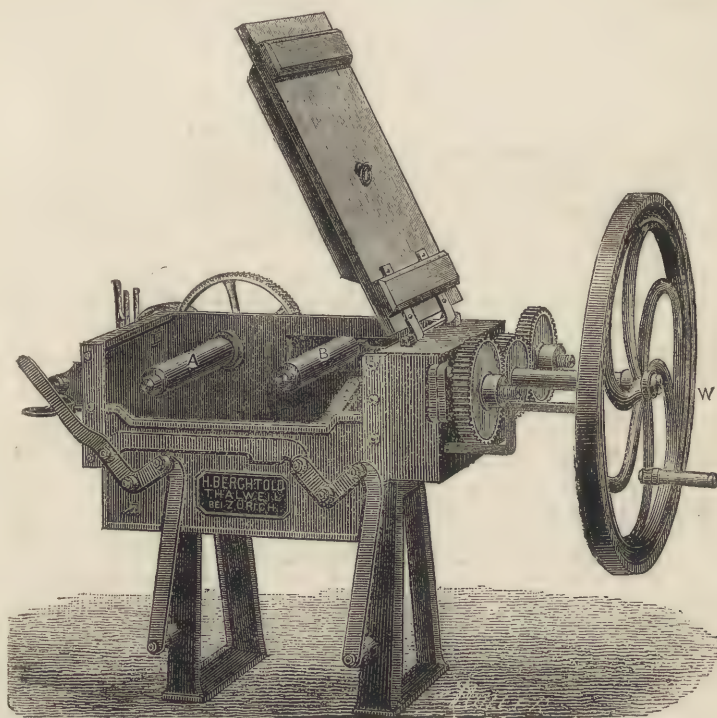


Fig. 51.—Silk lustring machine.

arrangement, the bobbins, B, are turned two or three times round the axis, *c*, first to the right, then to the left, thus giving the hanks a sharp twist in each direction. After the bobbins, B, have been round twice, once to the right and once to the left, they resume their original position. While they are temporarily at rest, the upper bobbins, A, turn slightly round, changing slightly the position of the hank, and the twisting goes on again; and so on until the required gloss has been obtained. Levers, *d*, are provided for lifting the heavy weights, in removing the hanks, and replacing them by fresh ones.

The machine is also sometimes used for cotton yarn.

3. Lustreing.—The object of this operation is to impart to the silk the highest possible degree of lustre. This is effected by a simultaneous stretching and steaming in a machine like that shown in Fig. 51. The hanks are placed on the polished steel rollers, A and B; the lid is closed, steam is admitted to the box, and the hanks subjected to tension by drawing back the roller, B, by means of the wheel, W. During the operation both rollers revolve in the same direction. In some lustreing machines the rollers are hollow and can be heated by steam.

Bleaching of Silk.—Silk is usually bleached like wool, with sulphurous acid. The stoving is repeated from three to eight times, according to the quality of the silk, washing with water intervening between each stoving. Finally, it is washed well in water and “dyed white,” or tinted with various colours (generally coal-tar colours), according to the desired shade.

Bleaching with liquid sulphurous acid or with bisulphite of soda has, according to M. Moyret,* not hitherto met with any success.

The bleaching may also be effected by means of peroxide of hydrogen by a method similar to that described under wool. Better results are obtained, according to H. Koechlin, by the addition of burnt magnesia to the bath.

Lunge recommends a treatment with peroxide of hydrogen after stoving, for the purpose of destroying the sulphurous acid retained by the fibre; at the same time the purity of the white is increased.

Silk may also be bleached by treatment in a luke-warm solution of permanganate of potash, and subsequently in sulphurous acid or sulphite of soda.

TUSSUR SILK.

Tussur silk is ungummed or discharged like ordinary silk. After ungumming it is not white, but of a brown colour, which cannot be got rid of by the ordinary process of stoving. The colour may be partially removed by a treatment in permanganate of potash and magnesium sulphate, followed by a bath of sulphurous acid.

Better results seem to be attained by the method proposed by Tessié du Motay, which consists in working the silk for about an hour in a bath heated to 90 °C., and containing 50 to 100 per cent. barium peroxide on the weight of the silk. It is then passed through dilute hydrochloric acid, and washed.

An ammoniacal solution of peroxide of hydrogen may also serve for bleaching Tussur, the treatment being similar to that described for wool. Here, also, an addition of burnt magnesia to the bath may be made with advantage.

The following method has been proposed by Girard:—The silk is

* *Mon. de la teinture*, 1891, p. 225.

first treated with hydrochloric acid, then with a solution of soda or caustic soda at 3° Tw. The bleaching is then effected by steeping the silk for twenty-four hours in a weak solution of ammonium hypochlorite, prepared by double decomposition from bleaching-powder and ammonium carbonate or sulphate. The treatment with ammonium hypochlorite is repeated, if necessary. The silk is then passed through dilute hydrochloric acid, and washed.

Tussur silk can only be bleached to a light cream. In consequence of the great degree of resistance which the fibre shows towards chemical reagents, more severe treatments might be employed with advantage for bleaching it than those usually suggested.

PART V.

ACIDS, ALKALIES, MORDANTS, &c.

THE drugs which are used by the dyer are, as a rule, divided into three groups :—

1. Chemicals generally.
2. Mordants.
3. Dyestuffs.

This division is based on the practical applications of the materials in question ; but it is not correct, even from a merely practical point of view. Potassium bichromate for example, which is generally called a mordant, acts as a dyestuff in the production of chrome yellow, and it might also be classed amongst the members of the first group, on account of its being used as an oxidising agent or for other purposes. It is still more difficult to give a theoretically satisfactory definition of the three groups.

Under *Chemicals* will be understood those materials which are employed in the preparing of the textile goods before dyeing—for instance, for bleaching—and which are required during the processes of dyeing and finishing, *without, however, becoming part of the colour* either entirely or in part.

Mordants.—The name is derived from the French word *mordre* (to corrode), because the early French dyers believed that the utility of the metallic salts they employed consisted in their corrosive nature ; it was believed that these substances opened the pores of the textile fibres and thus rendered them more capable of absorbing the dyestuffs. At a later period it was recognised that the so-called mordants entered into a chemical combination with the dyestuffs and formed insoluble compounds, or “colour lakes ;” hence these substances were considered principally as fixing agents for the dyestuffs. In many cases this is true—*i.e.*, where a dyestuff dyes without the aid of mordants, and becomes simply faster to washing and milling by the application of the mordant. In most cases, however, the mordant is an essential constituent of the colour, as without it no colour at all or only a worthless shade is produced. We consider as mordants substances which, partly or wholly, combine with the dyestuffs to form definite compounds in the fibre, thus distinguishing them from those chemicals which take part in the dyeing process without entering the ultimate colour.

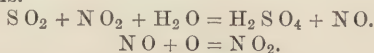
Chemically there is no essential difference between the members of the first and the second group ; hence they will be described together in this chapter without being formally separated, but their

applications in mordanting and dyeing will be dealt with specially in subsequent paragraphs.

The *Dyestuffs* will be treated in separate chapters (*q.v.*), since their chemical and tinctorial characters differ greatly from those of the other substances in use by the dyer.

ACIDS.

Sulphuric Acid (Oil of Vitriol), $\text{H}_2\text{SO}_4 = \text{SO}_2(\text{OH})_2$.—Sulphuric acid is produced on the large scale by allowing sulphur dioxide, nitrous gases, air, and aqueous vapour to react on each other in leaden chambers. The nitrous fumes simply act as carriers of oxygen, and the process may be considered to take place according to the following equations.



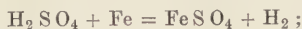
The acid which collects in the chambers is known as *chamber acid* and has a specific gravity of 1.54–1.60. By further concentration in leaden pans, or in the Glover-tower, a brown coloured acid with a sp. gr. of 1.69–1.73 and a strength of 76–80 per cent. H_2SO_4 is obtained, which is known as *brown oil of vitriol* (B. O. V.). This acid is further concentrated in vessels of glass, platinum, or iron, and thus the commercial *concentrated sulphuric acid* or *oil of vitriol* (O. V. or D. O. V., *i.e.*, double O. V.) is produced; this product contains, however, 2 to 3 per cent., and even as much as 7 per cent. water. Stronger acid, corresponding to the formula H_2SO_4 (the so-called *monohydrate*), is obtained by mixing the commercial article with sulphur trioxide (fuming sulphuric acid).

Sulphuric acid is a thick oily liquid without colour or smell, which possesses a sp. gr. of about 1.838 at 15° and boils at 338°; it begins, however, to distil at 290°, and is thereby partially decomposed into sulphur trioxide and water. The acid becomes solid below 0°, and melts again at 10°·5.

Sulphuric acid absorbs water with great avidity and with evolution of great heat. The greatest care has to be observed in mixing it with water, that it does not boil up: *water should never be poured into strong sulphuric acid; the acid should always be allowed to flow into the water slowly and in a thin stream with stirring, and even then the water must not be hot.* Sulphuric acid which has been diluted with half its weight of water does not give off great heat on being further diluted. The acid may absorb moisture from the air, and, by increasing in volume, may overflow the vessels in which it is contained, but when it is diluted with water, the resulting volume of the mixture is less than the sum of the volumes of the acid and water before mixing (measured at the same temperature). The mixture undergoes contraction, and the contraction is greatest when the liquids are in the proportion of one molecule of acid to two molecules of water.

Sulphuric acid is, under ordinary conditions, the strongest acid we

possess. It forms salts with all metals, and displaces, in most cases, other acids which are combined with bases. It is a dibasic acid and forms either neutral salts like Na_2SO_4 or acid salts like NaHSO_4 . The salts of sulphuric acid are called the *sulphates*; the acid salts are known as *bisulphates* or *acid sulphates*. Sulphuric acid dissolves most of the metals; it either forms salts with them, as is, for instance, the case when the dilute acid acts on iron or zinc, hydrogen being evolved:



or it dissolves the metal by a complicated process, when a part of the acid is reduced to sulphurous acid which escapes, while no hydrogen is liberated; this is the case when the strong hot acid acts on copper:



Iron is dissolved by diluted sulphuric acid, but an acid of 1.65 sp. gr. or more has no effect on this metal; hence strong acid can be further concentrated or transported in iron vessels; hence, too, many chemical processes in which sulphuric acid is used are effected in iron vessels.

Sulphuric acid extracts the elements of water from many substances; thus many organic compounds—*e.g.*, sugar, starch, or vegetable fibres—are entirely decomposed and charred (*carbonised*), while others are otherwise chemically changed.

Commercial sulphuric acid contains both a varying amount of water and several other impurities, notably arsenic, selenium, lead, iron, sulphur dioxide, or nitrous gases. In addition, the acid is often coloured by organic dust which has been charred by the liquid. The commercial product, however, is usually pure enough for the requirements of the dyer.

In the following the term “sulphuric acid” will always refer to the concentrated acid of 168° Tw.

The strength of sulphuric acid is determined by titration with normal alkali (see under *Analysis*). For an approximate estimation it is sufficient to ascertain the specific gravity with a hydrometer. Sulphuric acid of 98 per cent. H_2SO_4 possesses the highest specific gravity; the density of the liquid decreases on further concentration, and the monohydrate shows about the same density as an acid containing 95 per cent. H_2SO_4 .

PERCENTAGE AND SPECIFIC GRAVITY OF SULPHURIC ACID AT 15° C. (*Otto*).

Per cent. by weight. H_2SO_4 .	Specific Gravity.	Per cent. by weight. SO_3 .	Per cent. by weight. H_2SO_4 .	Specific Gravity.	Per cent. by weight. SO_3 .	Per cent. by weight. H_2SO_4 .	Specific Gravity.	Per cent. by weight. SO_3 .
1	1.0064	0.816	11	1.0756	8.980	21	1.1516	17.14
2	1.0130	1.630	12	1.0830	9.790	22	1.1590	17.95
3	1.0190	2.445	13	1.0910	10.61	23	1.1670	18.77
4	1.0256	3.260	14	1.0980	11.42	24	1.1740	19.58
5	1.0320	4.080	15	1.1060	12.24	25	1.1820	20.40
6	1.0390	4.890	16	1.1136	13.06	26	1.1900	21.22
7	1.0464	5.710	17	1.1210	13.87	27	1.1980	22.03
8	1.0536	6.530	18	1.1290	14.69	28	1.2066	22.85
9	1.0610	7.340	19	1.1360	15.51	29	1.2150	23.67
10	1.0680	8.160	20	1.1440	16.32	30	1.2230	24.49

SPECIFIC GRAVITY OF SULPHURIC ACID AT 60° F. (15½° C.)

(Lunge and Isler).

Degrees Twaddle.	100 parts by weight contain		Kilo. per Litre. H ₂ SO ₄ .	Degrees Twaddle.	100 parts by weight contain		Kilo. per Litre. H ₂ SO ₄ .	Degrees Twaddle.	100 parts by weight contain		Kilo. per Litre. H ₂ SO ₄ .
	SO ₃ .	H ₂ SO ₄ .			SO ₃ .	H ₂ SO ₄ .			SO ₃ .	H ₂ SO ₄ .	
40	22.30	27.32	0.328	86	43.36	53.11	0.759	132	60.11	73.64	1.222
41	22.82	27.95	0.337	87	43.75	53.59	0.769	133	60.46	74.07	1.233
42	23.33	28.58	0.346	88	44.14	54.07	0.779	134	60.82	74.51	1.244
43	23.84	29.21	0.355	89	44.53	54.55	0.789	135	61.20	74.97	1.256
44	24.36	29.84	0.364	90	44.92	55.03	0.798	136	61.57	75.42	1.267
45	24.88	30.48	0.373	91	45.31	55.50	0.808	137	61.93	75.86	1.278
46	25.39	31.11	0.382	92	45.69	55.97	0.817	138	62.29	76.30	1.289
47	25.88	31.70	0.391	93	46.07	56.43	0.827	139	62.64	76.73	1.301
48	26.35	32.28	0.400	94	46.45	56.90	0.837	140	63.00	77.17	1.312
49	26.83	32.86	0.409	95	46.83	57.37	0.846	141	63.35	77.60	1.323
50	27.29	33.43	0.418	96	47.21	57.83	0.856	142	63.70	78.04	1.334
51	27.76	34.00	0.426	97	47.57	58.28	0.866	143	64.07	78.48	1.346
52	28.22	34.57	0.435	98	47.95	58.74	0.876	144	64.43	78.92	1.357
53	28.69	35.14	0.444	99	48.34	59.22	0.886	145	64.78	79.36	1.369
54	29.15	35.71	0.454	100	48.73	59.70	0.896	146	65.14	79.80	1.381
55	29.62	36.29	0.462	101	49.12	60.18	0.906	147	65.50	80.24	1.392
56	30.10	36.87	0.472	102	49.51	60.65	0.916	148	65.86	80.68	1.404
57	30.57	37.45	0.481	103	49.89	61.12	0.926	149	66.22	81.12	1.416
58	31.04	38.03	0.490	104	50.28	61.59	0.936	150	66.58	81.56	1.427
59	31.52	38.61	0.500	105	50.66	62.06	0.946	151	66.94	82.00	1.439
60	31.99	39.19	0.510	106	51.04	62.53	0.957	152	67.30	82.44	1.451
61	32.46	39.77	0.519	107	51.43	63.00	0.967	153	67.65	82.88	1.463
62	32.94	40.35	0.529	108	51.78	63.43	0.977	154	68.02	83.32	1.475
63	33.41	40.93	0.538	109	52.12	63.85	0.987	155	68.49	83.90	1.489
64	33.88	41.50	0.548	110	52.46	64.26	0.996	156	68.98	84.50	1.504
65	34.35	42.08	0.557	111	52.79	64.67	1.006	157	69.47	85.10	1.519
66	34.80	42.66	0.567	112	53.12	65.08	1.015	158	69.96	85.70	1.534
67	35.27	43.20	0.577	113	53.46	65.49	1.025	159	70.45	86.30	1.549
68	35.71	43.74	0.586	114	53.80	65.90	1.035	160	70.94	86.90	1.564
69	36.14	44.28	0.596	115	54.13	66.30	1.044	161	71.50	87.60	1.581
70	36.58	44.82	0.605	116	54.46	66.71	1.054	162	72.08	88.30	1.598
71	37.02	45.35	0.614	117	54.80	67.13	1.064	163	72.69	89.05	1.621
72	37.45	45.88	0.624	118	55.18	67.59	1.075	164	73.51	90.05	1.639
73	37.89	46.41	0.633	119	55.55	68.05	1.085	165	74.29	91.00	1.661
74	38.32	46.94	0.643	120	55.93	68.51	1.096	166	75.19	92.10	1.685
75	38.75	47.47	0.653	121	56.30	68.97	1.107	167	76.27	93.43	1.713
76	39.18	48.00	0.662	122	56.68	69.43	1.118	167 ⁶ / ₁₀	77.23	94.60	1.739
77	39.62	48.53	0.672	123	57.05	69.89	1.128	167 ⁶ / ₁₀	77.55	95.00	1.748
78	40.05	49.06	0.682	124	57.40	70.32	1.139	168	78.04	95.60	1.759
79	40.48	49.59	0.692	125	57.75	70.74	1.150	168 ⁶ / ₁₀	79.19	97.00	1.786
80	40.91	50.11	0.702	126	58.09	71.16	1.160	168 ⁶ / ₁₀	79.76	97.70	1.799
81	41.33	50.63	0.711	127	58.43	71.57	1.170	168 ⁶ / ₁₀	80.16	98.20	1.808
82	41.76	51.15	0.721	128	58.77	71.99	1.181	168	80.98	99.20	1.825
83	42.17	51.66	0.730	129	59.10	72.40	1.192	167 ⁸ / ₁₀	81.39	99.70	1.834
84	42.57	52.15	0.740	130	59.45	72.87	1.202	167 ⁸ / ₁₀	81.59	99.95	1.838
85	42.96	52.63	0.750	131	59.78	73.23	1.212				

The number of pounds of H₂SO₄ per gallon is found by multiplying the number in the fourth column by 10 (kilo. per litre).

Sulphuric acid is the most important of all chemical products, and is manufactured on an enormous scale. It may be said that our whole civilisation is dependent on this substance; most chemical industries and many other trades use it extensively; in the production of dye-stuffs and other materials which are indispensable in dyeing, it cannot be replaced. It is used in bleaching, mordanting, and dyeing, for the carbonising of woollen materials, &c.

Fuming or *Nordhausen sulphuric acid* is sulphuric acid containing varying quantities of *sulphur trioxide* or *sulphuric anhydride*, S O_3 .

Sulphur Dioxide, S O_2 .—Sulphur dioxide is the product of the combustion of sulphur. It is produced on the large scale by burning sulphur or sulphur ores; in the laboratory from sulphuric acid by heating the latter with charcoal, sulphur, or copper shavings. Sulphur dioxide is a colourless gas, possessing the characteristic suffocating smell of burning sulphur; it is 2.21 times heavier than air, and can be reduced by cold (-15°C.) or by pressure (30 lbs. per sq. in.) to a colourless liquid which boils at 8°C. It is brought into commerce in this compressed form, which is very convenient for use in the laboratory. Sulphur dioxide is very soluble in water; the saturated solution contains per volume

at 0° :	68.86	volumes S O_2 ,	sp. gr.	1.061.
„ 10° :	51.38	„ S O_2 ,	„	1.055.
„ 20° :	36.21	„ S O_2 ,	„	1.024.

The solution of the gas in water may be considered to contain *sulphurous acid*, $\text{H}_2 \text{S O}_3$.

Sulphur dioxide does not sustain respiration; neither animals nor plants can live in an atmosphere containing comparatively small amounts of the gas. It does not support combustion, and hence, is sometimes used in extinguishing fires.

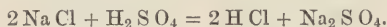
Sulphur dioxide has considerable affinity for oxygen, combining with it in the free state with the aid of finely-divided platinum at high temperatures (as in the process for manufacturing sulphuric anhydride). The solution of the gas slowly absorbs oxygen from the air, and forms sulphuric acid. Sulphur dioxide is also oxidised by compounds that contain much oxygen; bichromate of potash, for instance, is converted into chromium sulphate, and permanganate into manganous sulphate. On the other hand, it is reduced to sulphur by sulphuretted hydrogen, $\text{S O}_2 + 2 \text{S H}_2 = 3 \text{S} + 2 \text{H}_2 \text{O}$.

Sulphur dioxide possesses in the presence of water reducing properties, of which use is made in bleaching. According to the equation, $\text{S O}_2 + 2 \text{H}_2 \text{O} = \text{H}_2 \text{S O}_4 + \text{H}_2$, hydrogen is liberated, in presence of many coloured organic compounds, which are thereby transformed into colourless soluble substances. Since the latter oxidise in the air and regenerate the original colouring matter, washing must follow the bleaching to remove these substances entirely. Thus sulphur dioxide-

is used in gaseous form and in solution for bleaching wool and silk, straw, feathers, &c.; bisulphites are applied in a similar way.

Sulphurous Acid, $\text{H}_2\text{S O}_3 = \text{S O (O H)}_2$, which is known only in solutions, is the hydrate of sulphur dioxide. It is a dibasic acid, and forms neutral salts or *sulphites* (monosulphites), like $\text{Na}_2\text{S O}_3$; and acid salts or *bisulphites*, like Na H S O_3 . *Metasulphite* (or pyrosulphite) of potassium and of sodium, contain one equivalent of water less than the corresponding bisulphite, $\text{Na}_2\text{S}_2\text{O}_5 = 2\text{Na H S O}_3 - \text{H}_2\text{O}$.

Hydrochloric Acid, H Cl (*Muriatic acid*; *spirits of salt*).—Hydrochloric acid is obtained by the decomposition of sodium chloride (common salt) with sulphuric acid according to the equation:



Enormous quantities are produced in this way as a bye-product in the manufacture of soda by the "Le Blanc process."

In the pure state, hydrochloric gas is a colourless gas which fumes strongly in moist air, has a penetrating smell, and dissolves readily in water.

Hydrochloric acid (*i.e.*, the aqueous solution) when pure is a colourless liquid. The concentrated acid has at 15°C . the sp. gr. of 1.212, and contains 43 per cent. hydrochloric acid gas, some of which is gradually given off into the atmosphere with the evolution of white fumes. When distilled it loses gas until it is diluted to a certain strength that varies with the pressure. At the ordinary atmospheric pressure, a liquid distils which boils at a constant temperature of 110° , has the sp. gr. 1.101, and contains 20.2 per cent. (by weight) of hydrochloric acid gas.

Hydrochloric acid is one of the strongest acids, and replaces most other acids in their compounds. It is a monobasic acid, and forms salts, which are called *chlorides*—*e.g.*, sodium chloride, Na Cl . Most of these salts are readily soluble in water. Hydrochloric acid dissolves many metals with evolution of hydrogen, and dissolves most metallic oxides and hydroxides. Lead is attacked by hot hydrochloric acid; hence lead-lined vessels and leaden pipes cannot be used in working with this acid. Hydrochloric acid is oxidised by the higher oxides, such as manganese dioxide, lead dioxide, nitric or chromic acid, &c., the hydrogen combining with oxygen to form water and chlorine being liberated; on this fact depend both the process of producing chlorine from the acid with the aid of manganese dioxide and the energetic action of *aqua regia*.

Commercial hydrochloric acid contains iron, arsenic, sulphuric acid, and organic matter, and has a yellow colour; it is generally pure enough for technical purposes. The commercial product has a sp. gr. of 1.12 to 1.19; it is shipped in glass carboys, or in large earthenware pots.

The strength of hydrochloric acid is determined by acidimetric ti-

tration (see under *Analysis*) or, roughly, by the hydrometer, the specific gravity increasing with the strength (see following Table). Hydrochloric acid is next to sulphuric acid and soda, the most important chemical product. It is not used extensively in the dye-house, but it can be employed in many cases when sulphuric acid is used. It is used in great quantities for the preparation of dyers' materials.

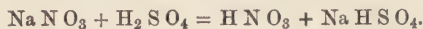
SPECIFIC GRAVITY OF HYDROCHLORIC ACID AT 15° C., COMPARED WITH WATER AT 4° C. AND REDUCED TO VACUUM.

(Lunge and Marchlewsky).

Degrees Twaddle.	Specific Gravity at 4° in vacuo.	100 Parts by weight contain parts by weight of H Cl.	1 Litre contains grms. H Cl.*	Degrees Twaddle.	Specific Gravity at 4° in vacuo.	100 Parts by weight contain parts by weight of H Cl.	1 Litre contains grms. H Cl.*
0	1.000	0.16	1.6	21	1.105	20.97	232
1	1.005	1.15	12	22	1.110	21.92	243
2	1.010	2.14	22	23	1.115	22.86	255
3	1.015	3.12	32	24	1.120	23.82	267
4	1.020	4.13	42	25	1.125	24.78	278
5	1.025	5.15	53	26	1.130	25.75	291
6	1.030	6.15	64	27	1.135	26.70	303
7	1.035	7.15	74	28	1.140	27.66	315
8	1.040	8.16	85	29	1.145	28.61	328
9	1.045	9.16	96	30	1.150	29.57	340
10	1.050	10.17	107	31	1.155	30.55	353
11	1.055	11.18	118	32	1.160	31.52	366
12	1.060	12.19	129	33	1.165	32.49	379
13	1.065	13.19	141	34	1.170	33.46	392
14	1.070	14.17	152	35	1.175	34.42	404
15	1.075	15.16	163	36	1.180	35.39	418
16	1.080	16.15	174	37	1.185	36.31	430
17	1.085	17.13	186	38	1.190	37.23	443
18	1.090	18.11	197	39	1.195	38.16	456
19	1.095	19.06	209	40	1.200	39.11	469
20	1.100	20.01	220				

* The number of pounds H Cl contained in a gallon is found by dividing the number in the fourth column (grms. H Cl per litre) by 100. It may be noticed that each degree Twaddle indicates approximately 1 per cent. H Cl.

Nitric Acid, $\text{H N O}_3 = \text{N O}_2 (\text{O H})$.—Nitric acid is manufactured by the decomposition of sodium nitrate by sulphuric acid.



It is a colourless liquid possessing a slight smell, and fumes strongly in the air. It has a sp. gr. of 1.53, and boils at 86° with partial decomposition into nitrogen peroxide, oxygen, and water; acid containing 32 per cent. water (sp. gr. 1.414) boils without decomposition. Nitric acid is a very strong monobasic acid, the salts of which are known as *nitrates*. It dissolves most metals, thereby forming salts which are

generally soluble in water; during the reaction, a part of the acid is generally reduced to lower oxides of nitrogen and even to elementary nitrogen and ammonia. Iron is not attacked by concentrated nitric acid, but moderately diluted nitric acid (of a sp. gr. above 1.12) dissolves it to ferric nitrate, while a weaker acid forms ferrous nitrate and ammonium nitrate.

Nitric acid is a powerful oxidising agent, and many organic substances are ignited when moistened with the same, *e.g.*, straw and sawdust, while some almost explode in contact with the same, *e.g.*, alcohol and turpentine. The concentrated acid is also extremely corrosive to the skin, and may produce deep and painful wounds; the diluted acid colours the skin, wool, silk, feathers, and many other organic substances yellow.

Commercial nitric acid contains lower oxides of nitrogen by which it is coloured slightly yellow, and, in addition, small amounts of chlorine and iodine, which were present in the nitrate, as also iron, sulphuric acid, and sodium nitrate and sulphate. The strength varies from 1.35 to 1.44 sp. gr.

Aqua fortis is impure nitric acid which contains a considerable amount of the lower oxides of nitrogen. The ordinary commercial nitric acid is also frequently called aqua fortis.

The strength of nitric acid is determined by acidimetric titration or by the hydrometer (see following Table).

SPECIFIC GRAVITY OF NITRIC ACID AT 15° C., COMPARED WITH WATER OF 4° C. AND REDUCED TO VACUUM (*Lunge and Rey*).

Degrees Twaddle.	Per cent. H N O_3 by weight.	Degrees Twaddle.	Per cent. H N O_3 by weight.	Degrees Twaddle.	Per cent. H N O_3 by weight.	Degrees Twaddle.	Per cent. H N O_3 by weight.	Degrees Twaddle.	Per cent. H N O_3 by weight.
0	0.10	21	17.89	42	33.82	63	49.89	84	69.80
1	1.00	22	18.67	43	34.55	64	50.71	85	70.98
2	1.90	23	19.45	44	35.28	65	51.53	86	72.17
3	2.80	24	20.23	45	36.03	66	52.37	87	73.39
4	3.70	25	21.00	46	36.78	67	53.22	88	74.68
5	4.60	26	21.77	47	37.53	68	54.07	89	75.98
6	5.50	27	22.54	48	38.29	69	54.93	90	77.28
7	6.38	28	23.31	49	39.05	70	55.79	91	78.60
8	7.26	29	24.08	50	39.82	71	56.66	92	79.98
9	8.13	30	24.84	51	40.58	72	57.57	93	81.42
10	8.99	31	25.60	52	41.34	73	58.48	94	82.90
11	9.84	32	26.36	53	42.10	74	59.39	95	84.45
12	10.68	33	27.12	54	42.87	75	60.30	96	86.05
13	11.51	34	27.88	55	43.64	76	61.27	97	87.70
14	12.33	35	28.63	56	44.41	77	62.24	98	89.60
15	13.15	36	29.38	57	45.18	78	63.23	99	91.60
16	13.95	37	30.13	58	45.95	79	64.25	100	94.09
17	14.74	38	30.88	59	46.72	80	65.30	101	96.39
18	15.53	39	31.62	60	47.49	81	66.40	102	98.10
19	16.32	40	32.36	61	48.26	82	67.50	103	99.07
20	17.11	41	33.09	62	49.07	83	68.63	104	99.67

Nitric acid finds an extensive application in the arts; for example, in the production of sulphuric acid, nitroglycerin, and most artificial dyestuffs. Dyers do not use it much in the free state, except for the preparation of certain mordants; but salts and other products of nitric acid are of great importance in the dye-house.

Acetic Acid, $C_2H_4O_2 = CH_3CO(OH)$.—*Glacial Acetic Acid*—*Pyroligneous Acid*—*Vinegar*.—Acetic acid is produced by the destructive distillation of wood, and by the acetous fermentation of alcohol and alcoholic liquors (beer, wine, &c.). The pure concentrated acid is called glacial acetic acid because it freezes when cooled, thereby forming an ice-like mass. It is produced from pure acetates (obtained from wood-tar). Pyroligneous acid is a crude acetic acid obtained by neutralising wood-tar with lime, and decomposing the resulting salt with sulphuric acid. Vinegar, finally, is the product of acetous fermentation of alcoholic liquids.

Pure acetic acid (glacial acetic acid) is a colourless substance which possesses a penetrating acid smell, and a strong acid taste. It forms a crystalline mass of 1.105 sp. gr., which melts at $17^\circ C$. and boils without being decomposed at $118^\circ C$. It is hygroscopic, and mixes with water and with alcohol in all proportions; in mixing with water contraction and increase of specific gravity takes place; a mixture containing 77 per cent. acetic acid and 23 per cent. water, corresponding to the formula $C_2H_4O_2 + H_2O$, has the highest specific gravity (1.075 at 15.5°); while a mixture of about equal weights of acid and water has the same specific gravity as the pure acid. In determining the concentration of strong acid with the hydrometer, this fact must be taken into account. Acetic acid is a well-defined monobasic acid, the salts of which are called *acetates*. All normal acetates are soluble in water.

Concentrated acetic acid dissolves many organic substances, also sulphur and phosphorus. The acid neutralises basic oxides completely; but it does not prevent or affect many chemical processes, as the strong inorganic acids and oxalic acid do; further it does not attack the vegetable fibre neither in solutions, nor on drying, nor in steaming. For these reasons acetic acid is largely used in dyeing.

Commercial Acetic Acid.—Pure glacial acetic acid is chiefly used for scientific or pharmaceutical purposes. Diluted more or less impure acetic acid, produced from acetate of lime, is used for technical purposes. It contains generally about 29 per cent. $C_2H_4O_2$, and possesses a sp. gr. of 1.04 ($=8^\circ Tw.$); the impurities of this acid consist chiefly of empyreumatic substances. The data in this book refer to the commercial acetic acid of 29 per cent. $C_2H_4O_2$.

Pyroligneous acid contains considerably more empyreumatic substances than the previous article, and these exert a strong reducing action (they decolorise potassium permanganate). The pyroligneous acid is preferable for its reducing power in many cases, as, for instance,

for the preparation of pyrolignite of iron, because it prevents a premature oxidation of the iron, for which reason it is frequently employed instead of the purer commercial product (see under *Analysis*).

The hydrometer cannot be used with advantage for the estimation of acetic acid; for a reliable valuation, the acidimetric titration is necessary.

SPECIFIC GRAVITY OF ACETIC ACID AT 15° C. (*Oudemans*).

Specific Gravity.	Per Cent. C ₂ H ₄ O ₂ .	Specific Gravity.	Per Cent. C ₂ H ₄ O ₂ .	Specific Gravity.	Per Cent. C ₂ H ₄ O ₂ .	Specific Gravity.	Per Cent. C ₂ H ₄ O ₂ .
0.9992	0	1.0363	26	1.0631	52	1.0748	77
1.0007	1	1.0375	27	1.0638	53	1.0748	78
1.0022	2	1.0388	28	1.0646	54	1.0748	79
1.0037	3	1.0400	29	1.0653	55	1.0748	80
1.0052	4	1.0412	30	1.0660	56	1.0747	81
1.0067	5	1.0424	31	1.0666	57	1.0746	82
1.0083	6	1.0436	32	1.0673	58	1.0744	83
1.0098	7	1.0447	33	1.0679	59	1.0742	84
1.0113	8	1.0459	34	1.0685	60	1.0739	85
1.0127	9	1.0470	35	1.0691	61	1.0736	86
1.0142	10	1.0481	36	1.0697	62	1.0731	87
1.0157	11	1.0492	37	1.0702	63	1.0726	88
1.0171	12	1.0502	38	1.0707	64	1.0720	89
1.0185	13	1.0513	39	1.0712	65	1.0713	90
1.0200	14	1.0523	40	1.0717	66	1.0705	91
1.0214	15	1.0533	41	1.0721	67	1.0696	92
1.0228	16	1.0543	42	1.0725	68	1.0686	93
1.0242	17	1.0552	43	1.0729	69	1.0674	94
1.0256	18	1.0562	44	1.0733	70	1.0660	95
1.0270	19	1.0571	45	1.0737	71	1.0644	96
1.0284	20	1.0580	46	1.0740	72	1.0625	97
1.0298	21	1.0589	47	1.0742	73	1.0604	98
1.0311	22	1.0598	48	1.0744	74	1.0580	99
1.0324	23	1.0607	49	1.0746	75	1.0553	100
1.0337	24	1.0615	50	1.0747	76		
1.0350	25	1.0623	51				

Note.—The specific gravities above 1.0553 correspond to two liquids of different strength. To find whether a certain solution contains more or less than 77 per cent. C₂ H₄ O₂ (which mixture possesses the highest specific gravity) a little water may be added; if the specific gravity increases, the acid was above 77 per cent., otherwise below this strength.

Oxalic Acid, $\text{H}_2\text{C}_2\text{O}_4 = \begin{Bmatrix} \text{CO}(\text{OH}) \\ \text{CO}(\text{OH}) \end{Bmatrix}$. — Oxalic acid is manufactured by heating sawdust with caustic potash and soda; it can be obtained by the oxidation of many organic substances, and occurs in the juice of many plants in the form of potassium- and calcium-salts.

Oxalic acid crystallises in prisms which have the composition $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$; the crystals lose their water of crystallisation at 100° C. It can be sublimated by careful heating to 150° to 160° C., and is decom-

posed by higher temperatures. The crystals dissolve at ordinary temperatures in about eight times their weight of water (see table below), at 90° they dissolve in one third their weight of water. The acid is not acted upon by nitric acid or chlorine, but it is oxidised by potassium permanganate, and by manganese peroxide in acid solution forming carbon dioxide.

Oxalic acid is a strong dibasic acid, and forms neutral salts, so-called *oxalates*, and acid salts or *binoxalates*. The alkaline oxalates are soluble in water; most of the other oxalates are insoluble. The neutral oxalate of calcium is insoluble both in water and in acetic or oxalic acid, but readily soluble in hydrochloric or nitric acid.

Oxalic acid and the oxalates are poisonous. The commercial article is nearly pure acid. The acid is estimated by acidimetric or oxidimetric (permanganate) titration (see under *Analysis*).

Oxalic acid is used largely in dyeing.

SPECIFIC GRAVITY OF SOLUTIONS OF OXALIC ACID,
 $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ at 15° (Franz).

Specific Gravity.	Per Cent. $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$	Specific Gravity.	Per Cent. $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$	Specific Gravity.	Per Cent. $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$
1·0032	1	1·0182	6	1·0271	10
1·0064	2	1·0204	7	1·0289	11
1·0096	3	1·0226	8	1·0309	12
1·0128	4	1·0248	9	1·0320	12·6
1·0160	5				

Tartaric Acid, $\text{H}_6\text{C}_4\text{O}_6 = \begin{cases} \text{CO}(\text{OH}) \\ \text{CH}(\text{OH}) \\ \text{CH}(\text{OH}) \\ \text{CO}(\text{OH}) \end{cases}$. — (*Ordinary Tartaric*

Acid, *Dextro-tartaric Acid*).—Tartaric acid exists both in the free state and in the form of salts in the juice of many fruits (grapes), and is deposited as potassium salt or tartar during the fermentation of wine; the acid is obtained from the crude tartar.

Tartaric acid forms large transparent prisms of strong and pure acid taste, which melt at 170° C., and are decomposed by higher temperatures without distilling; it is easily soluble in water, but less so in alcohol. Tartaric acid is a strong dibasic acid; its salts are known as *tartrates*. The commercial article is nearly pure; it contains some sulphuric acid, lime, and other metallic oxides.

Tartaric acid is estimated by acidimetric titration (see under *Analysis*).

SPECIFIC GRAVITY OF TARTARIC ACID SOLUTIONS
AT 15° C. (*Gerlach*).

Specific Gravity.	Per Cent. $C_4H_6O_6$.	Specific Gravity.	Per Cent. $C_4H_6O_6$.	Specific Gravity.	Per Cent. $C_4H_6O_6$.
1·0045	1	1·0969	20	1·2078	40
1·0090	2	1·1072	22	1·2198	42
1·0179	4	1·1175	24	1·2317	44
1·0273	6	1·1282	26	1·2441	46
1·0371	8	1·1393	28	1·2568	48
1·0469	10	1·1505	30	1·2696	50
1·0565	12	1·1615	32	1·2828	52
1·0661	14	1·1726	34	1·2961	54
1·0761	16	1·1840	36	1·3093	56
1·0865	18	1·1959	38	1·3220	(saturated) 57·9

Tartaric acid is frequently employed in dyeing and printing, both in the free state and in the form of the potassium salt (tartar). It is chiefly used as an addition to the mordant bath in wool dyeing and for brightening colours on silk after dyeing, as also as a resist and discharge in printing.

Citric Acid, $H_8C_6O_7 = C_3H_4(OH)(CO_2H)_3$.—Citric acid exists in the juice of lemons, limes, oranges, and other fruits; it is obtained from the juice of lemons (or lime-fruit) which comes into commerce from southern Europe and the West Indies.

Citric acid crystallises in prisms with one molecule of water of crystallisation, $H_8C_6O_7 + H_2O$, which melt at 153° C.; it dissolves in three-quarters its weight of water at 15° C. and in twice its weight of alcohol.

Citric acid is a well-defined tribasic acid; the salts are known as *citrates*.

Commercial citric acid consists of large crystals which often show a yellowish tinge but do not contain any considerable quantity of impurities. A good acid should leave no ash when incinerated.

Citric acid is estimated by titration or by taking the specific gravity. It is used as a resist and discharge in printing.

Laevulinic Acid, $C_5H_8O_3 = CH_3COCH_2CH_2CO_2H$.—Laevulinic acid is produced by the action of acids on cane sugar, levulose, cellulose, starch, and other carbohydrates.

Laevulinic acid crystallises in scales which melt at 33° and boil at 239° C. It is very soluble in water and in alcohol. It is a monobasic acid.

At the present time laevulinic acid is used but little in calico printing; recently its employment as a solvent for induline has been patented by the Hoechst-Colour Works. It may possibly replace oxalic, tartaric, and citric acid in many cases.

Lactic Acid, $\text{H}_6 \text{C}_3 \text{O}_3 = \text{C} \text{H}_3 \text{C} \text{H} (\text{O} \text{H}) \text{C} \text{O}_2 \text{H}$ (*Ordinary* or *Ethylidene Lactic Acid*).—Lactic acid is generated by the so-called lactic fermentation of various kinds of sugar (cane sugar, sugar of milk, &c.), in the presence of albuminoid substances, especially of casein; it occurs in sour milk. It has recently been reported that a process has been found to produce it at a cheap price.

Lactic acid is not known in the pure state, it is obtained diluted with water as a syrupy liquid of 1.25 sp. gr., which cannot be distilled without decomposition. It is a monobasic acid; the salts are called *lactates*.

Lactic acid will probably become a valuable substitute for other organic acids in dyeing and printing, if it can be furnished at a low price; at the present time it is not used in these industries.

OIL-MORDANTS.

HIGHER FATTY ACIDS (FATTY OILS, FATS, &c.)

Palmitic Acid, $\text{C}_{16} \text{H}_{32} \text{O}_2 = \text{C}_{15} \text{H}_{31} (\text{C} \text{O} . \text{O} \text{H})$, is a white substance which melts at 62°C ., and can be distilled under diminished pressure without being decomposed. It is a monobasic acid, the salts of which are called *palmitates*. Potassium and sodium palmitates are the chief constituents of palm oil soap; they are decomposed by water. (See *Soap*). The other salts are insoluble in water.

Palmitin or *Tripalmitin*, $(\text{C}_{16} \text{H}_{31} \text{O}_2)_3 \text{C}_3 \text{H}_5$, is the glycerin ether of palmitic acid. It occurs in most animal fats, in olive oil and in palm oil, and melts at 66°C . Palmitin is decomposed into glycerin and palmitic acid, or a palmitate, on being heated with sulphuric acid, alkalis, lime, or superheated steam. The process of decomposition with alkali of this and similar ethers is called *saponification* and the resulting salt *soap*. (See below.) Palmitic acid is used by dyers in the form of soap.

Stearic Acid, $\text{C}_{18} \text{H}_{36} \text{O}_2 = \text{C}_{17} \text{H}_{35} (\text{C} \text{O} . \text{O} \text{H})$.—Stearic acid closely resembles palmitic acid. It is a white substance which melts at 69°C . and can be distilled under diminished pressure without being decomposed. It is a monobasic acid, and its salts are called *stearates*. These salts have the same properties as the palmitates.

Stearin or *Tristearin*, $(\text{C}_{18} \text{H}_{35} \text{O}_2)_3 \text{C}_3 \text{H}_5$, the glycerin ether, melts at 72°C ., and yields the acid by saponification. Stearin occurs in all solid animal fats, and is best prepared from mutton-fat or shea-butter.

Stearic acid is one of the chief constituents of ordinary soap.

Oleic Acid, $\text{C}_{18} \text{H}_{34} \text{O}_2 = \text{C}_{17} \text{H}_{33} (\text{C} \text{O} . \text{O} \text{H})$.—Oleic acid is obtained as a bye-product in the manufacture of stearic acid, and can be prepared

by saponification of oleïn, its glycerin ether, which is the chief constituent of olive oil. Oleïc acid is a colourless oil which melts at $14^{\circ}\text{C}.$, but which cannot be volatilised without undergoing decomposition. It is a monobasic acid, and forms salts which are called *oleates* and resemble the palmitates and stearates.

Oleïc acid contains two atoms of hydrogen less than stearic acid, and can be converted into this compound by the action of hydrogen in the nascent state, $\text{C}_{18}\text{H}_{34}\text{O}_2 + 2\text{H} = \text{C}_{18}\text{H}_{36}\text{O}_2$. It readily takes up two atoms of iodine or bromine and forms di-iod- or dibrom-stearic acid; for instance, $\text{C}_{18}\text{H}_{34}\text{O}_2 + \text{I}_2 = \text{C}_{18}\text{H}_{34}\text{I}_2\text{O}_2$. By oxidation with potassium permanganate in alkaline solution it is transformed into dioxystearic acid, $\text{C}_{18}\text{H}_{34}(\text{OH})_2\text{CO}_2\text{H}$. While in the pure state it possesses neither colour, taste, nor smell, and does not act on litmus; by the oxidising action of the air it turns yellow and acid and acquires a rancid smell. It possesses in an eminent degree the property of absorbing oxygen. According to Camille Koechlin, oleïc acid takes up under the influence of light 300 to 400 times its volume of oxygen from the atmosphere. Oleïc acid is converted by nitrous acid into the isomeric *elaidic* acid, $\text{C}_{18}\text{H}_{34}\text{O}_2$, which melts at $45^{\circ}\text{C}.$ Oleïc acid in form of the sodium or potassium salt is a constituent of many soaps, especially of olive-oil soap. In the form of oleïn it is a very important material for the production of Turkey red.

Oleïn or *Trioleïn*, $(\text{C}_{18}\text{H}_{33}\text{O}_2)_3\text{C}_3\text{H}_5$, the glycerin ether of oleïc acid, is present in most fatty oils, and forms, as already stated, the chief constituent of olive oil. It melts at $6^{\circ}\text{C}.$

The glycerin ethers of palmitic, stearic, and oleïc acids are the chief constituents of most animal and vegetable fats and fatty oils—in contrast with the ethereal oils. As oleïn is a liquid, while palmitin and stearin are solid, the fluidity or hardness of such fatty oils and fats depends upon the larger or smaller percentage of oleïn they contain. These glycerin ethers cannot be distilled without undergoing decomposition whereby the glycerin is converted into acroleïn, $\text{C}_3\text{H}_4\text{O}$, a volatile liquid possessing a powerful penetrating smell (the smell of burnt fat). The fats are resolved into the corresponding acids and glycerin when heated with very dilute sulphuric acid, caustic alkalies, or alkaline earths, and by the action of steam; even by the action of moist air they are partially decomposed in this way, thus becoming “rancid.” The alkali-salts of these acids form the essential constituents of soap, and for this reason the process of splitting fats into acids and glycerin by alkalies and by other agents is called “saponification.” The lead salts of these three acids are obtained by boiling fats with lead oxide and water; they are not soluble in water, and are called “lead plasters.” The lead plasters serve as mordants for some dyestuffs (for example, the eosins). The fibre is first impregnated with a solution of soap and subsequently with a lead salt.

The fatty oils are separated into the drying and non-drying oils;

the drying oils differing from the others in becoming dry and resinous from oxidation in the air. This change depends upon the presence of glycerides of oleic and similar acids—*i.e.*, acids which contain less than twice as many atoms of hydrogen as of carbon. Many drying oils contain the glycerin ether of *linoleic acid*, $C_{16}H_{28}O_2$. The different kinds of *wax* are related to the fats, being ethers of fatty acids and of monovalent higher alcohols; *beeswax*, for instance, is the palmitic ether of melissyl alcohol, $C_{30}H_{62}O$.

Ricinoleic Acid (*Oxyoleic acid*), $C_{18}H_{34}O_3 = C_{17}H_{32}(O H)(C O_2 H)$, is a white crystalline mass which melts at 16° to 17° C. The glycerin ether, *ricinolein*, $(C_{18}H_{33}O_3)_3C_3H_5$, is the chief constituent of castor oil, and yields the acid on saponification.

Ricinoleic acid takes up two equivalents of hydrogen, bromine, or iodine, &c., analogously to oleic acid. Both acids are unsaturated compounds, and possess in a high degree the property of becoming polymerised, thereby forming compounds of a greater molecular weight. The products of polymerisation play an important part in the production of Turkey red, and will be referred to again.

Ricinoleic acid is an oxyoleic acid, and differs from oleic acid in its behaviour towards sulphuric acid. Ricinoleic acid probably forms a true sulphuric ether by actual etherification, whereas oleic acid is not etherified in the usual way, although it probably also yields a true sulphate. (See below.)

Turkey-red Oil, Alizarin Oil, Sulphated Oil, Soluble Oil or Olein.—These names apply to products which are obtained by the action of sulphuric acid on vegetable oils at the ordinary temperature. Olive oil, cotton-seed oil, and possibly some other oils may be used to some extent, but, practically, castor oil alone is the raw material used in the preparation of the sulphated oil of the cotton dyer and printer. The process of manufacture, as it takes place on the large scale, has recently been described by various writers* in conformance with other reports. Castor oil is slowly and thoroughly mixed (from 12 to 24 hours) with the proper quantity of concentrated sulphuric acid, the temperature not being allowed to rise above 40° C. Sulphuric acid, to the extent of from 15 to 40 per cent. of the weight of the oil, is used, in winter more acid being required than in summer. The mixture is allowed to stand until a sample poured into distilled water yields a clear solution, when it must be washed at once, as the product readily decomposes. The product is washed with a solution of common salt, or Glauber's salt, to remove the excess of free acid, and it is finally partially neutralised and diluted to the required strength. The heat is not allowed to rise too high, otherwise the evolution of considerable quantities of sulphur dioxide takes place, and a dark coloured product is obtained, which gives unsatisfactory results in

* J. A. Wilson, *Journ. Soc. Dyers and Col.*, 1891, p. 94; P. Lochtin, *ibid.*, 1890, p. 82.

dyeing. But in any case some sulphur dioxide is perceived by its smell, which probably results from the decomposition of the albuminoids and other extraneous matter in the oil. Soda or ammonia is used for neutralising, and the oil is diluted with water, so as to make a finished product containing 45 to 50 per cent. fatty matter (unless it is kept stronger to save expense of freight). J. A. Wilson gives the following average composition:—

20 to 27	per cent.	free fatty acids,
25	„	combined acid and glycerides,
1.30 to 1.50	„	Na ₂ O.

Fremy was the first who studied the action of sulphuric acid on fatty oils in detail; and Runge (*Farben Chemie*, 1834) recognised already the value of the sulphated olive oil, and recommended its employment in dyeing.* The firm of Gros, Roman, Marozeau & Co., in Wesserling, employed the product during the early sixties for the fixation of aniline dyestuffs; and, later, it was also used for goods to be printed with alizarin (*E. Lauber, H. Schmid*).† The processes remained secret, and the results were not very satisfactory, since the goods acquired a yellowish tint on steaming, which could not be removed by bleaching. The introduction of sulphated castor oil was a great improvement, and this article is now used almost exclusively for Turkey-reds, alizarin-reds, and print goods (except in the production of Turkey-reds by means of rancid Gallipoli oil). Sulphated castor oil had been already used for some time by some firms before it was brought into the market (almost simultaneously) by an English and a French house. In 1876 John M. Sumner & Co., of Manchester, introduced the sodium salt of sulphated castor oil, invented by Dr. Wuth in Ramsbottom; and P. L'Honoré, of Havre, manufactured the corresponding ammonium salt discovered by Fr. Storck. A. Mueller-Jacobs manufactured sulphated castor oil at an early date in Russia, and claims to have taken part in the discovery.‡ The composition of sulphated oil has been the object of several investigations, but has not been cleared up as yet.

The first detailed publication was made by Liechti and Suida.§ The correctness of their results is in doubt, and therefore we shall not state them in full. According to these authors a compound ether of the oil and sulphuric acid is formed, having the following constitution:—



* The firm Braun & Cordier, in Rouen, used as early as 1846 a product which was obtained by the action of nitric acid on olive oil for the preparation of Turkey-reds. The process was invented by Hirn. (Persoz, *Traité d'Impression*; Henry Schmid, *Dingler's Polyt. Journ.*, 250, p. 513.)

† *Dingler's Polyt. Journ.*, 247, p. 11; *Ib.*, 250, p. 543.

‡ *Germ. Patent*, 1488, Sept. 30, 1877; *Dingler's Polyt. Journ.*, 254, p. 302.

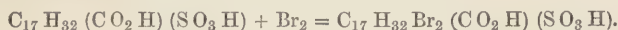
§ *Journ. Soc. Chem. Ind.*, 1833, p. 537.

while oxidised acids are also obtained, viz., from olive oil or oleic acid, $C_{18}H_{34}O_3$, and from castor oil or ricinoleic acid, $C_{18}H_{34}O_5$.

The oxygen required for the production of such oxyacids was furnished by the reduction of sulphuric acid to sulphur dioxide, a considerable amount of which escaped during the process. Since in the production of commercial sulphated oil the evolution of sulphur dioxide is strenuously avoided, Liechti and Suida's researches do not explain the usual process. A. Mueller-Jacobs* prepared sulphated oil by the action of sulphuric acid on olive oil; the temperature was not allowed to rise beyond $32^\circ C.$, and *not the least trace of sulphur dioxide was evolved in his process.* The action of sulphuric acid on castor oil was not thoroughly studied by him. He obtained from olive oil a sulphated oleic acid, $C_{18}H_{34}SO_5$, which, according to the analysis of the lead salt and barium salt, was a dibasic acid, and to which he ascribes the constitution $C_{17}H_{32}\left\{\begin{smallmatrix} SO_3H \\ CO_2H \end{smallmatrix}\right\}$. This product he asserts, in accordance with all later investigators (but contrary to Liechti and Suida), yields no trace whatever of glycerin on decomposition, so that the reaction of sulphuric acid on olive oil or triolein is to be explained, according to this author, by the equation—



The sulphated oleic acid takes up two equivalents (*i.e.*, atoms) of bromine or iodine.



A part of the sulphated acid undergoes decomposition during the process by splitting off sulphuric acid and taking up water—thus, according to Mueller-Jacobs, from $C_{17}H_{32}(CO_2H)(SO_3H)$ and water, oxyoleic acid, $C_{17}H_{32}(CO_2H)(OH)$, oxystearic acid, $C_{17}H_{34}(CO_2H)(OH)$, and sulphuric acid are formed, together with the sulphated acid, as products of the reaction. The equation by which he explains this decomposition is faulty,† and no correct explanation has been given, although H. Schmid‡ has called attention to his error of calculation. Since the exact compositions of substances, like oxyoleic and oxystearic acid, present slight differences only, exact results have not been ascertainable by analysis, so that it remains an open question whether these substances have been obtained at all by Mueller-Jacobs. This author found that there always remained a considerable amount of unmodified triolein in the product of the reaction, which dissolves in the mixture of acids; and he ascribes to this triolein the mordanting effect of the sulphated oil, whereas the acids act simply as solvents or carriers of the active substance. He

* *Journ. Soc. Chem. Ind.*, 1884, p. 412.

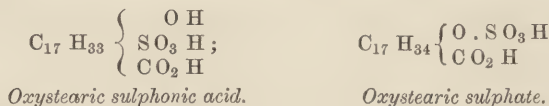
† $2C_{18}H_{34}SO_5 + H_2O = C_{18}H_{34}O_3 + C_{18}H_{36}O_3 + 2H_2SO_4$ (!?).

‡ *Dingler's Polyt. Journ.*, 254, p. 346.

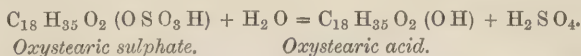
asserts that sulphated oleic acid, prepared by the action of sulphuric acid on pure oleic acid, did not give a good Turkey-red, but such was obtained when 10 per cent. of triolein was added to the sulphated oleic acid. *This fact may be correct for sulphated oil made from olive oil or oleic acid; but, as will be seen later, no inferences must be made therefrom on the behaviour of preparations from castor oil or ricinoleic acid.*

R. Benedict* has prepared the true sulphuric acid of a higher fatty acid, in order to ascertain whether the compounds belonging to this group of bodies behaved similarly to the Turkey-red oil acids soluble in water. The compound, which could not be obtained in the pure state, is, in many respects, similar to the Turkey-red oil acid; but the two are essentially different from each other in this respect: the sulpho-fatty acid is not decomposed by concentrated hydrochloric acid, even at a high temperature; while the acid from Turkey-red oil is easily decomposed, even by dilute hydrochloric acid, into sulphuric acid and oxystearic acid.

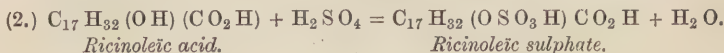
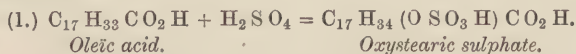
Turkey-red oil is, therefore, not a true sulphonic acid; it belongs, according to its whole behaviour, to the class of sulphuric ethers. The difference of constitution is made apparent by the two following formulæ for sulphated oil from olive oil:—



Mueller-Jacobs, however, states (see above) that he obtained an oleic sulphonic acid $\left(\text{C}_{18} \text{H}_{34} \text{O}_5 \text{S} = \text{C}_{17} \text{H}_{32} \left\{ \begin{array}{l} \text{S O}_3 \text{H} \\ \text{C O}_2 \text{H} \end{array} \right\} \right)$ which takes up two atoms of bromine; while, at the present time, the soluble part of Turkey-red oil from olive oil (and from oleic acid) is generally described as the saturated oxystearic sulphate ($\text{C}_{18} \text{H}_{36} \text{S O}_6$). This compound is decomposed by acids, according to the equation:

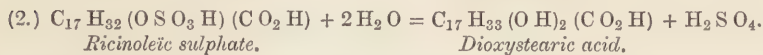
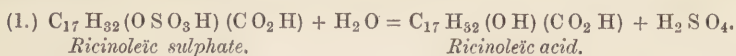


Ricinoleic acid differs essentially from oleic acid inasmuch as it contains a hydroxyl group in addition to the carboxyl group. When sulphuric acid acts on triricinolein (castor oil) or on ricinoleic acid, it does not form a sulphate by addition, as is believed to be the case with triolein, &c., but it acts on the hydroxyl group; a true etherification takes place with the separation of water, and a non-saturated compound is formed:



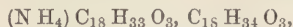
* *Journ. Soc. Dyers and Col.*, 1888, p. 44.

The ricinoleic sulphate may lose its sulphuric acid with or without the addition of water :



The decomposition of the ricinoleic sulphate proceeds principally or entirely according to the first equation, and results in the formation of ricinoleic acid, which is disposed to polymerise and oxidise. Indeed, the most recent investigations of Juillard and of Scheurer-Kestner * indicate that Turkey-red oil (from castor oil) contains the sulphuric ethers of ricinoleic acid and of several polyricinoleic acids, mixed with the products of their decomposition, among which ricinoleic acid predominates. The presence of glycerin in the commercial oil is incontestable ; but it is unnecessary to make it enter into the composition of the body, as it is easily eliminated without any modification of the properties of the oil.

P. Lochtin (*l.c.*) considers the ordinary Turkey-red oil as a mixture of (insufficiently neutralised) sulpho-fatty acids and fatty acids ; he ascribes but a subordinate importance to the sulpho-compounds in Turkey-red oil. He prepared an acid ammonium ricinoleate which had a composition corresponding nearly to the formula



and obtained in experimental dye-trials with this so-called *acid soap*, a more even, fuller, and purer shade than in dyeing with the Turkey-red oil. The reasons why castor-oil soap (with soda), now frequently applied instead of Turkey-red oil, produces inferior results, are to be found in the fact that the solution of the soap is much more frothy than that of the neutralised sulphated oil ; and chiefly, because the dyed material shows the flat and dirty shade of the alkali alizarate. This last fact is explained by the suggestion that in mordanting with alumina a waterproof envelope—ricinoleate of alumina—is formed externally on the fibre, thus enclosing the nucleus of the alkali soap. As good results as with Turkey-red oil were obtained with the soap solution by modifying in the first place the method of clearing, which was continued after boiling under pressure with weak solutions of the lime salts (gypsum, calcium chloride, calcium nitrate, &c.) ; in order to avoid the injurious influence of the soda as much as possible, Lochtin added sulphuric acid so as to neutralise $\frac{1}{2}$ to $\frac{3}{4}$ of the alkali present (which did not separate the fatty acid from the solution). He further prepared the above-mentioned ammoniacal oil soap and found that material oiled with this soap contains little alkali after drying, and in the alkaline

* *Journ. Soc. Dyers and Col.*, 1891, p. 69.

clearing produces results not inferior to those obtained with Turkey-red oil.

There is some difference between the Turkey-red oil and the acid soap. The material prepared with ammoniacal Turkey-red oil shows an acid reaction after drying, the ammonium salt being decomposed and the sulpho-fatty acid producing sulphuric acid; while, on the other hand, the material oiled with the ammoniacal acid soap shows, after drying, a neutral or faintly alkaline reaction.

Scheurer-Kestner (*l.c.*) prepared a Turkey-red oil in the following manner:—One part sulphuric acid (96 per cent.) and three parts castor oil were mixed slowly, so as not to allow the temperature to rise more than a few degrees. The mixture was allowed to stand for 12 hours, and washed with 5 parts of water at 40°C. 3.7 parts Turkey-red oil were thus obtained. It was still further purified for the following investigation by washing with solutions of sodium sulphate.

The oil consists of two substances; the one (about two-thirds of the mixture) is soluble in water, and is a sulphated compound; the other (about one-third) is not sulphated. The oil never contained any unchanged castor oil. To separate the oil into the sulphated and non-sulphated compounds, it was dissolved in ether and water added to the ethereal solution; the former is taken up by the water, while the latter is retained by the ether. (See below.)

The Turkey-red oil (the mixture of the two substances) is heavier than water; it is very soluble in water, giving a fluorescent solution with an acid reaction, and is precipitated unchanged by sodium sulphate. If allowed to stand for several days in contact with water at the ordinary temperature it does not decompose at all; hence it is more stable than generally supposed. On boiling with twice its weight of water it becomes milky at first, but it soon separates completely into an aqueous liquid and an oil, which floats at the top. The supernatant liquid is entirely free from mineral acid; all the latter is dissolved by the water.

When Turkey-red oil is dissolved in ether, and water is added to the ethereal solution, the latter becomes milky, and gives a white precipitate. This reaction has been attributed to a decomposition of the substance dissolved by the ether; but, on addition of more water, the precipitate re-dissolves, forming a clear, syrupy liquid, which, on addition of sulphate of soda, yields the unchanged sulphated fatty acid, while the ether contains non-sulphated fatty acid.

Scheurer-Kestner believes that the sulphated compound when dissolved in water exists in the hydrated state, containing 16.4 per cent. water. Dehydration takes place when it is taken up by the ether, and, on addition of water, an insoluble anhydrous compound is precipitated at first, which, however, becomes soluble by hydration. Turkey-red oil, as it comes into commerce, or as it is obtained by the previous method, is always hydrated according to this author.

The non-sulphated portion is very acid, and must be either ricinoleic acid or a polymerised derivative. It is lighter than water, insoluble in water, free from the elements of sulphuric acid, dissolves readily in caustic soda, and is precipitated without alteration by sulphuric acid. The other part of the oil is heavier than water, and gives a perfectly clear solution with water without fluorescence. Fluorescence only exists when the soluble and insoluble oil are re-united; in this case the light oil dissolves in the other, and communicates this property to it. The soluble oil contains the elements of sulphuric acid in the proportion corresponding to 8.5 per cent. SO_3 . It dissolves in caustic soda, and is re-precipitated by sulphuric acid without alteration. It is strongly hydrated, and when dehydrated by means of a slight heat, it thickens till it acquires about the consistency of wax. Precipitated from its aqueous solution by sulphate of soda, it is combined with 30 to 40 per cent. water, which it gradually loses on being heated to 75° ; toward 80° it colours slightly, becomes turbid, and loses 5 to 6 per cent. more water. Its titration corresponds exactly to the amount of SO_3 it contains. The solution of the sulphated oil in water decomposes within a few hours at 80° ; but it is entirely unaffected by atmospheric conditions, and does not decompose at the ordinary temperature. It is only heat which decomposes it. The light oil is not affected by heat.

As to the brightening properties of the two substances, they are remarkable for their difference; for whilst the insoluble oil imparts to alizarin pink a crimson, the soluble oil gives it a yellow shade.

Scheurer-Kestner's oil contained, according to this author, no unmodified oil. Wilson, whose analysis has been previously given, states that the commercial article contains such. The percentage of unmodified oil depends both on the temperature and on the quantity of acid which have been employed in sulphating. Scheurer-Kestner has presumably worked in his laboratory at a not very low temperature, and used a comparatively large—although not excessive—quantity of sulphuric acid. On the large scale the amount of acid used never suffices to sulphonate the whole quantity of castor oil, a large excess being required to attain this end. Theoretically, nearly 1 part sulphuric acid is required for 3 parts castor oil—the quantity used by Scheurer-Kestner; and this may be further reduced by one-third, since one-third of the product is not sulphated. But in practice even smaller quantities of sulphuric acid are used, and a considerable amount of what is used is not taken up in the process. From our present knowledge on the subject, we may consider the commercial Turkey-red oil as a mixture of ricinoleic sulphate, ricinoleic acid, and unmodified castor oil; possibly products of polymerisation, sulphated glycerin ethers, dioxy stearic acid, and other compounds are also present.

Turkey-red oil is used in Turkey-red (alizarin red) dyeing, as a

mordant for basic colours in cotton dyeing, for preparing calico before printing, in oiling wool, and in the finishing of cotton goods. Its alkaline solution acts like a soap, and is sometimes used as such.

TANNIN-SUBSTANCES AND ALLIED COMPOUNDS.

A number of organic acids are found in the vegetable kingdom which resemble each other by their chemical constitution, and by a similar behaviour in their reactions. Their most prominent property is the formation of a mechanical compound with hide, known as leather. In science, however, a number of compounds which lack, nearly or even entirely, the property of converting skin into leather are classified with the so-called tannin-substances, and it is difficult to give an exact and complete definition of this term.

In general the tannin-substances are characterised by a very astringent taste, by a feeble acid reaction towards litmus, by the property of precipitating albumen and gelatine from their aqueous solutions, and by producing either blue-black or green colourations with ferric acetate. These properties, however, do not belong exclusively to them, but are shared with other compounds.

The tannin-substances are carboxylic acids of the aromatic series ; in general, those which give blue-black colourations with ferric acetate are derivatives of pyrogallol and gallic acid, while those which afford a green colour are derived from catechol and protocatechuic acid. They are amorphous or subcrystalline solids possessing an astringent taste, more or less soluble in water, readily soluble in alcohol and in mixtures of alcohol and ether and in ethyl acetate, but nearly insoluble in ether ; in bisulphide of carbon, chloroform, petroleum spirit, and benzene they are insoluble ; and, in general, they are not readily soluble in dilute sulphuric acid. Most of them can be completely extracted from their aqueous solutions by the animal skin (rasped hide or hide powder), and give with solutions of gelatine precipitates similar to leather. They form precipitates with the acetates of the heavy metals, such as those of aluminium, copper, chromium, iron, lead, tin, and zinc, with tartar emetic and with stannous and stannic salts. With the sulphates, chlorides, and nitrates no precipitates are obtained since the tannates do not form in presence of free mineral acids. In addition they form insoluble compounds with organic bases—*e.g.*, the alkaloids of the cinchonas and with the basic dyestuffs. The tannin-substances are powerful reducing agents ; they precipitate the noble metals from their solutions in the metallic state, and possess a strong tendency, especially in alkaline solution, to absorb oxygen ; the oxidation products are, as a rule, strongly coloured.

The tannin-substances are largely employed in the "tanning" of leather, in dyeing, in medicine, and for the preparation of pyrogallol, gallic acid, inks, dyestuffs, &c. Their application in dyeing is based

on the fact that they are readily absorbed by the textile fibres, notably by cotton, linen, and silk; and on the property of forming insoluble compounds in the fibres, on the one hand with the heavy metals and with antimony, and on the other hand with the basic dyestuffs. In wool dyeing a special use is made of their property of precipitating certain impurities from the dye-bath so as to prevent these from being taken up by the fibre.

The following notes state briefly the character of the most important compounds connected with the tannin-substances.

Catechol or **Pyrocatechin**.—*Orthodioxypybenzene*, $C_6H_4(OH)_2$, is formed by the dry distillation of those tannin-substances which yield green colourations with ferric acetate and by fusing orthophenol-sulphonic acid with caustic potash. It may also be produced from guaiacol. It forms short white rhombic prisms, melts at 104° , boils at $245^\circ C.$, and is very soluble in water, in alcohol, and in ether. It produces a green colouration with ferric acetate, which becomes violet on the addition of ammonia; and it possesses strong reducing properties. The alkaline solutions become coloured by absorbing oxygen from the air.

Guaiacol, $C_6H_4(OH)(OCH_3)$, is the methyl-ether of catechol, and is a constituent of wood-tar. Small quantities are also present in pyroligneous acid.

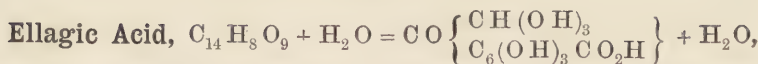
Protocatechuic Acid, $C_6H_3(OH)_2CO_2H$. $[(OH):(OH):(CO_2H) = 1:2:4]$, is obtained by fusing catechu and other organic substances with caustic potash. It resembles catechol.

Pyrogallol or **Pyrogallie Acid**, $C_6H_3(OH)_3$. $[OH = 1:2:3]$, is formed by dry distillation of gallic acid. It crystallises in white tablets or needles, melts at $131^\circ C.$, and can be sublimated and distilled without decomposition. It is freely soluble in water, in alcohol, and in ether. It gives a blue-black colouration with ferric salts, and has very strong reducing properties; the alkaline solution rapidly absorbs oxygen from the air, being thereby coloured. It is used for the quantitative determination of oxygen in the free state, and as a developer in photography. Pyrogallol is the mother substance of those tannin-substances which are coloured blue-black by ferric salts, and of several important dyestuffs—*e.g.*, gallein and coerulein.

Phloroglucol or **Phloroglucin**, $C_6H_6O_3 + 2H_2O$, is isomeric with pyrogallol, and is probably the symmetrical trioxybenzene, $C_6H_3(OH)_3$. It is obtained by fusing catechu, maclurin, quercitin, and other tannin-substances with caustic potash. Phloroglucol forms rhombic tablets which lose their water of crystallisation at 100° , and melt at 209° to $218^\circ C.$ It is readily soluble in water and in alcohol, but more so in ether; and has a very sweet taste. It does not give precipitates with metallic salts, except with basic lead acetate; with ferric chloride it gives a deep violet colouration. It is readily oxidisable, like the preceding substances.

Gallic Acid or **Trioxibenzoic Acid**, $C_6H_2(OH)_3(CO_2H) + H_2O$. $[(OH):(OH):(OH):(CO_2H) = 1:2:3:5]$, is formed by hydrolysis of tannic acid, $C_{14}H_{10}O_9 + H_2O = 2C_7H_6O_5$. It is prepared by subjecting crushed gall-nuts in water to fermentation, or by boiling tannic acid with diluted sulphuric acid. The product is obtained from the aqueous solution by evaporating and recrystallising. Gallic acid occurs in gall-nuts, sumach, divi-divi, and other tannin-substances, which give a blue-black colouration with ferric salts. It is probably a product of the decomposition of the tannic acid contained in them. Gallic acid forms triclinic crystals of a silky lustre, which lose their water of crystallisation above 100° , and melt with decomposition at 210° to 220° C. It is soluble in 130 parts of cold and 3 parts of boiling water, the hot saturated solution becoming a pasty mass of crystals on cooling. At 15° C. 100 parts of absolute alcohol dissolve 28 parts, diluted alcohol less, and 100 parts ether $2\frac{1}{2}$ parts gallic acid. The aqueous solution has a slightly acid and astringent taste, and gradually decomposes on standing. Gallic acid is a monobasic acid, and forms crystallisable salts. The alkaline gallates are stable in the dry state; but in solution they rapidly absorb oxygen from the air, and become brown with formation of humoid substances. Tartar emetic precipitates, even from very dilute solutions, a white precipitate of antimony gallate. On addition of ferric chloride to an aqueous solution of gallic acid an intensely blue precipitate is formed, which dissolves in an excess of the reagent with a green colour. Ferrous sulphate in the absence of air gives a white precipitate in concentrated (not in diluted) solutions; the liquid becomes bright blue on exposure to the air, and deposits a black precipitate without being decolourised. The reducing action of gallic acid is less energetic than that of the preceding compounds; Fehling's solution is only slowly and imperfectly reduced, but the salts of the noble metals are reduced by gallic acid; and an acid solution of potassium permanganate is thereby decolourised, hydroufigallic acid, a derivative of anthracene, being formed. In contrast with tannic acid, no precipitate is formed by gallic acid in solutions of albumen, gelatine, organic bases, or starch, but a mixture of gum arabic and starch is precipitated. Gallic acid has no tanning properties, and is not absorbed by cotton. On being heated slowly to 210° to 230° C. it is decomposed, and pyrogallol is formed; when heated more rapidly, and up to 250° , other products, chiefly metagallic acid, $C_6H_4O_2$, are formed. Heated with sulphuric acid to about 140° , gallic acid is converted into rufigallic acid, $C_{14}H_8O_8$ (or hexaoxyanthraquinone). A mixture of gallic and benzoic acid dissolved in sulphuric acid yields, on heating, anthragallol, $C_{14}H_8O_3$ (or trioxyanthraquinone, anthracene-brown).

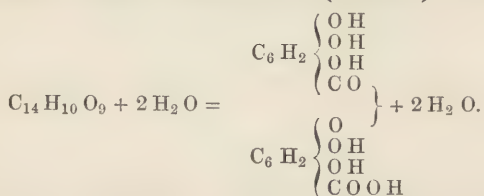
Gallic acid is employed in medicine, as a hair dye, in photography, and in the manufacture of certain colours (galloeyanin, gallein, &c.).



occurs in myrabolans, divi-divi, pomegranate rind, and other plant products, and is formed as a bye-product in the preparation of gallic acid. Ellagitannic acid on being heated in water to 110° C. forms ellagic acid. It is also found in bezoar stones (intestinal concretions of a Persian species of goat). Ellagic acid is little soluble in water or in alcohol, and insoluble in ether; it is without taste or smell, gives with ferric chloride, at first a green and then a blue-black colouration; the alkaline solution absorbs oxygen. Ellagic acid retains with great tenacity its water of crystallisation; it forms an anhydride, $C_{14}H_6O_8$, when heated to 120° C.

Phlobaphenes are the anhydrides of the various tannic acids formed by the loss of one or more equivalents of water. They are produced by boiling the solution of tannin-substances with dilute sulphuric acid, and are always present in the barks, &c., from which the tannin materials are obtained. They are brown amorphous bodies, sparingly soluble in water, ether, alcohol, alkalies, and alkaline carbonates. Their solubility in water depends much on their degree of hydration. The phlobaphenes are the colouring matters of the tannin-substances. They behave on the whole like the tannic acids themselves, colouring ferric salts, precipitating gelatine, and converting hide into leather. They are valuable tanning materials.

Tannic Acid or **Gallo-Tannic Acid (Tannin)**—*Digallic Acid*.—



It occurs in many tannin-substances, especially in gall-nuts, and in sumach. Gall-nuts contain, as a rule, 60 to 77 per cent. of it, and serve as raw materials for the manufacture of tannic acid. The gall-nuts are extracted with a mixture of water, alcohol and ether, and a solution, separated in two layers, is thus obtained; the bulk of the tannic acid is contained in the lower (aqueous) layer, and the tannic acid is prepared from this portion by evaporation. To obtain the tannin as a loose spongy mass, the syrupy solution of the same is mixed with some alcohol and ether, and then evaporated at a moderate temperature. The solution of tannin is caused to swell up by the escaping vapours, and is thereby formed as a loose and spongy mass, which is valued on account of its property of dissolving without difficulty. Tannic acid has also been produced by condensation of gallic acid, and (as stated above) has been resolved into gallic acid; hence it is proved that it is digallic acid— $2C_7H_6O_5 - H_2O = C_{14}H_{10}O_9$.

Tannic acid forms a colourless amorphous mass or light-yellowish to buff-coloured scales or brittle vitreous masses, and has a strongly astringent taste. It becomes yellowish in the light, even when air is excluded. On being heated, it darkens with or without melting; and at 215° C. it decomposes, pyrogallol and metagallic acid ($C_6H_4O_2$)—a black, amorphous, tasteless mass—being the chief products; when heated rapidly to 280° it forms metagallic acid only.

Tannic acid is soluble in 6 parts of cold water, and more freely in hot water; it is readily soluble in diluted, sparingly soluble in absolute alcohol; in absolute ether, carbon bisulphide, chloroform, petroleum spirit, and benzene it is nearly insoluble, but readily soluble in glycerin and in ethylacetate.

The aqueous solution of tannic acid gradually decomposes on standing. Tannic acid is precipitated from the strong aqueous solution by diluted sulphuric or hydrochloric acid, potassium, sodium, or ammonium chloride, potassium acetate, &c.; but not by nitric acid, nor by sodium sulphate. Skin and gelatine remove it completely from the aqueous solution. Tannic acid is a weak monobasic acid; it decomposes, however, the alkaline carbonates. The salts, which are known as *tannates*, are amorphous, and it is difficult to prepare them in the pure state; most of them are insoluble in water.

Tannic acid also forms insoluble compounds with the organic bases, albuminoid substances, gelatine, &c.

Tannic acid is readily oxidisable, and reduces the salts of the noble metals, of mercury and of copper, the permanganates, &c. The alkaline solution of tannic acid rapidly absorbs oxygen from the air, and acquires a brown colour by decomposition. If air is passed through a solution of tannic acid for a certain length of time, a yellow colouring matter—galloflavin—is produced. Ferrous sulphate gives in concentrated aqueous solutions a white precipitate which turns blue on access of the air. Ferric salts produce a bluish-black precipitate of ferric tannate or "ink;" the colour is destroyed by boiling or by reducing agents; the precipitate dissolves in hydrochloric acid, and is thrown down again by sodium acetate. An ammoniacal solution of cupric sulphate is precipitated by tannic acid; and Fehling's solution is reduced on heating, yellow or red cuprous oxide being formed. From a solution of cupric acetate, tannic acid precipitates green tannate of copper. With the soluble salts of antimony, bismuth, lead, tin, zinc, &c., white precipitates are formed which are soluble in acids. Tannic acid forms no precipitate with calcium acetate in the presence of acetic acid, and the solution remains clear on adding alcohol; by this reaction it can be separated from oxalic, tartaric, citric, and similar organic acids.

Tannic acid forms a white or buff-coloured flocculent precipitate with a solution of gelatine which is entirely insoluble in an excess of tannic acid, but not wholly insoluble in pure water; when freshly

formed it is often extremely finely divided ; but it is rapidly coagulated by ammonium chloride, alum, and other salts. This precipitate is considered to be the basis of leather ; but tannic acid itself is not a suitable material for tanning hides and producing leather. As stated before, tannic acid, on being heated above 200° , forms pyrogallol and metagallic acid ; on being heated with dry arsenic acid it produces ellagic acid ($C_{14}H_8O_9$) ; and a solution of tannic acid forms on boiling with ammonium sulphate gallaminic acid.

Tannic acid is used in pharmacy, in dyeing, and in printing, in the preparation of inks and dyestuffs, pyrogallol, gallic acid, &c.

SPECIFIC GRAVITY OF SOLUTIONS OF TANNIC ACID
AT 15° C. (*Trammer*).

Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.	Specific Gravity.	Per Cent. Tannic Acid.
1.0040	1.0	1.0084	2.1	1.0124	3.1	1.0164	4.1
1.0044	1.1	1.0088	2.2	1.0128	3.2	1.0168	4.2
1.0048	1.2	1.0092	2.3	1.0132	3.3	1.0172	4.3
1.0052	1.3	1.0096	2.4	1.0136	3.4	1.0176	4.4
1.0056	1.4	1.0100	2.5	1.0140	3.5	1.0180	4.5
1.0060	1.5	1.0104	2.6	1.0144	3.6	1.0184	4.6
1.0064	1.6	1.0108	2.7	1.0148	3.7	1.0188	4.7
1.0068	1.7	1.0112	2.8	1.0152	3.8	1.0192	4.8
1.0072	1.8	1.0116	2.9	1.0156	3.9	1.0196	4.9
1.0076	1.9	1.0120	3.0	1.0160	4.0	1.0200	5.0
1.0080	2.0						

Ellagitannic Acid, $C_{14}H_{10}O_{10}$, is contained in divi-divi, myrabolans, and as a glycoside in the rind of the pomegranate. It is a brown amorphous mass which is converted into its anhydride, ellagic acid, on being heated with water to 110° C. It yields a light brown precipitate with cupric acetate ; and with lead acetate in alcoholic solution a white precipitate of ellagitannate of lead. In general it strongly resembles tannic acid.

Quercitannic Acid, $C_{19}H_{16}O_{17}$ (?), is the tannin of oak-bark where it occurs, together with its own anhydride or phlobaphene, with gallic acid, ellagic acid, and various kinds of sugar. It can be prepared from oak-bark by successive extraction with alcohol, ether, and ethyl acetate, and forms a reddish-white amorphous powder, soluble in water, alcohol, and ethyl acetate, but not in ether or benzene.

Quercitannic acid gives a blue-black colour and, after some time, a precipitate with ferric chloride; it yields yellowish-white precipitates with albumen, gelatine, organic bases, and antimony salts; precipitates are also formed with lead acetate and ammoniacal solutions of zinc or magnesium chloride and of copper sulphate or acetate. The exact composition of quercitannic acid is not known; it is probably a derivative of gallic acid. Quercitannic acid loses water when heated to 130° to 140° C., and when boiled with very dilute sulphuric acid, as also with caustic alkalies or alkaline carbonates; and forms several anhydrides known as *phlobaphene*, *oak-bark red*, &c., which are brownish-red substances, sparingly soluble in water, but soluble in solutions of quercitannic acid. Their composition is very uncertain; they show the characteristic reactions of tannin-substances, and possess tanning properties. They are not employed in dyeing. Quercitannic acid and its anhydrides (in the form of oak-bark) are the most important materials for the tanning of leather.

Catechutannic Acid and **Mimotannic Acid** are probably identical substances. They are obtained from catechu and from gambier, but their composition is uncertain. They resemble tannic acid, but differ from it in the following reactions:—They yield greyish-green precipitates with ferric salts and no reactions with ferrous salts; with cupric sulphate they give a dense precipitate, but none with antimony salts. The composition of catechutannic acid has been stated to be $C_{21}H_{18}O_8$; it is a dark reddish-brown powder, soluble in water, alcohol, and ethyl acetate, but not in ether. The aqueous solution is precipitated by sulphuric acid, by albumen and gelatine.

Catechin, $C_{21}H_{20}O_9$, or $C_{21}H_{18}O_8$ (?), crystallises in small needles having the composition $C_{21}H_{20}O_9 + 5H_2O$. It is readily soluble in hot water, in alcohol, and in ethyl acetate, and moderately soluble in ether. It gives a green colouration with ferric chloride, has reducing properties, but does not give precipitates with organic bases or gelatine or antimony salts. Catechin occurs in catechu and in gambier; catechutannic acid is the first anhydride of catechin; other anhydrides are also known. The constitution of all these substances is uncertain. Catechin yields by decomposition catechol, protocatechuic acid and phloroglucol. When exposed to the air it is converted into a brown insoluble substance, known as *japonic acid*.

Description of the Tannins used in Dyeing.—A number of tannin-substances are employed as mordants in the dyeing of the textile fibres. Some of these substances are used on account of their lower price as substitutes for tannic acid in mordanting; hence they are here classified with this body as tannins. A number of tannin-substances, however (notably catechu), are not used as mordants, but as real colouring matters, hence they will not be included in the term "tannin" as here understood. Among the tannins sumach is next in importance to tannic acid, then follow myrabolans, valonia, divi-divi,

knopperrn, chestnut extract, quebracho, and others. Instead of pure tannic acid the extract of gall-nuts is also used. Tannic acid is most generally employed in mordanting cotton for bright shades, but sumach extract and myrabolans find increasing application for this fibre; the other tannins are chiefly used for the weighting of black silk.

Galls are the excrescences on plants, produced by the punctures of certain insects for the purpose of depositing their eggs.

(1) **Oak-Galls** are produced by the female gall-wasp (*Cynips gallæ tinctoriæ*, Oliv.), which drops an egg in the rind of young branches of certain oaks. A swelling (the gall-nut) is formed in which the young insect develops, and from which it finally escapes by piercing a hole through the shell. Those gall-nuts which are not pierced contain most tannic acid; they have a fresh green or blue colour, and are heavy—*green or blue galls*. If the insect has escaped, they are yellow and lighter and of inferior quality—*white galls*.

The best oak-galls are the *Aleppo galls*, which come from Persia or the East Indies *viâ* Aleppo, and the *Turkish or Levant galls* (Tripoli, Smyrna, Corea, &c., galls); they contain 55 to 60 per cent. tannic acid, and about 4 per cent. gallic acid. Greatly inferior are the Italian, Hungarian, French, and German galls.

The holes of worm-eaten galls are sometimes filled up with wax; by immersing them in boiling water, the wax will melt and the holes become visible. Extracted galls have been covered with a solution of ferrous sulphate, which is readily detected by the usual reactions for iron.

(2) **Chinese and Japanese Gall-Nuts** are produced by the sting of a plant-louse (*Aphis chinensis*, Doubl.) on the leaves and leaf-stalks of *Rhus semialata*. They are very light and hollow, and very rich in tannic acid (65 to 79, and even as much as 77 per cent.). The Japanese galls are smaller than the Chinese, and are more valued. Both are chiefly used for the production of tannic acid.

Knopperrn are galls formed by the sting of a gall wasp in the immature fruit of a species of oak growing in Austria. They contain from 25 to 35 per cent. tannic acid, and are largely employed in tanning, but are less suitable for dyeing than the other galls.

Tannic Acid, $C_{14}H_{10}O_9$. (See p. 170.)

Sumach consists of the leaves and twigs of several species of *Rhus*; the sumach from *Rhus coriaria* is the best, and Sicilian sumach is the finest commercial quality. Next come the Spanish, Portuguese, Greek, and Virginian (U.S.A.) sumachs; inferior qualities are the sumachs from Provence, Hungary, and Tyrol, which are derived from *Coriaria myrtifolia* and *Rhus cotinus*, and cannot replace the sumach from *Rhus coriaria*. Sumach is sold in the form of the whole or crushed leaves, or as a powder; the leaf-stalks and small twigs are often admixed. Best sumach contains 15 to 20 per cent. tannin, and has an olive-green colour and a fresh agreeable smell. The sumach, which is dull in

colour and smell, has been deteriorated by moisture and long keeping. Sumach contains some reddish colouring matter, which prohibits it from being employed for the dyeing of light and brilliant shades; the Sicilian sumach is the least coloured; it contains gallotannic acid.

Sumach Extract is manufactured in large quantities as a thick dark-brown liquid of about 52° Tw. Excellent qualities of decolourised sumach extract are now offered, which can replace tannic acid even for light shades.

Myrabolans are the fruits of several kinds of trees growing in China and the East Indies (*Terminalia chebula*, Willd.; *Myrabolanus chebula*, Gaert.). The dried fruits resemble a slightly shrivelled plum, are nearly an inch long, very hard, and possess a bitter astringent taste. The stones contain little tannin; the bulk is in the peel (25 to 45 per cent. in the whole fruit). The tannin of the myrabolans is ellagitannic acid. Myrabolans contain a yellowish-brown colouring matter, which, when removed, makes this material a good substitute for tannic acid in many applications. They are used in tanning, in cotton dyeing, and in the black dyeing of silk.

Divi-Divi or **Libi-Divi** are the leguminous fruits of a small tree (*Cesalpinia coriaria*, Willd.) found in the West Indies and South America. The pods are about 3 inches long, $\frac{1}{2}$ to $\frac{3}{4}$ inch broad, and very thin; they are often folded up in the shape of a letter S. They have a lustrous brown or blackish colour externally, and a yellowish one internally; the lightest coloured are the best. The tannin-substance is ellagitannic acid (19 to 35 per cent.); they also contain gallic acid. Divi-divi is used for tanning and black dyeing.

Valonia consists of the acorn cups of certain species of oak from Asia Minor, Greece, the Grecian Archipelago, and the South of France (*Quercus cegilops*, *Quercus græca*, and *Quercus vallonea*). They have a diameter up to $1\frac{1}{2}$ inches, and should possess a bright drab colour. Their tannin-substance is tannic acid (25 to 35 per cent. and sometimes more) accompanied by a dirty-yellow colouring matter.

Bablah or **Nebheb** are the leguminous fruits of several species of Acacia (*Acacia Arabica*—East Indian bablah, and *Acacia nilotica*—Egyptian bablah). The fruits contain nearly 20 per cent. tannin-substance. The extract has a sweetish, little astringent taste. Bablahs are used for tanning and for black dyeing.

Chestnut.—The extract is prepared from the wood of the chestnut-oak (*Æsculus hippo-castanum*). The composition of the tannin-substance is not known; it yields a green colouration with ferric chloride, precipitates gelatine solutions, and produces, when fused with caustic potash, protocatechuic acid and phloroglucin.

The wood contains 8 to 10 per cent. tannin. The solid extract has a brilliant black colour; the liquid extracts are brown syrups, possess an astringent taste, and smell like burnt sugar. On diluting

with water they become turbid and yield brown phlobaphenes, which apparently take part in the dyeing process. Chestnut extract is the most important tannin for the black dyeing of silk.

In the foregoing are named the principal tannin-substances used in mordanting and black-silk dyeing. A number of other similar bodies (catechu, gambier, kino, and fustic) will be described amongst the dyestuffs.

THE APPLICATION OF THE TANNIN-SUBSTANCES OR "TANNINS" TO THE TEXTILE FIBRES.

Application to Cotton and Linen.—Cotton and linen evince little power to attract and retain most dyestuffs so as to yield full and fast shades. They possess, however, the property of taking up and fixing considerable amounts of certain substances which are able to form insoluble compounds with dyestuffs. It cannot be decided whether the fibres exert a chemical action towards these substances; for, as yet, no proof of any affinity has been found.

Cotton and linen possess a remarkable power of attracting tannins from their aqueous solutions; the quantity which is taken up by the fibre from the liquor depends chiefly on the concentration of the latter and on the quantity of other substances, like sulphuric acid, common or Glauber's salt, &c., which may be present. According to Juste Koechlin, cotton, which has been saturated with a solution containing 50 grammes tannic acid per litre, still continues to absorb more tannin when steeped in a solution containing 20 grammes per litre only. It retains the whole of its tannic acid in a solution of 5 grammes per litre, and only begins to lose it in a solution of 2 grammes per litre. Acids and salts precipitate the tannin from its aqueous solutions, and, if added to the latter, cause them to be better exhausted.

The actual amounts of tannic acid taken up by cotton under various conditions have been determined by Knecht & Kershaw.*

In the experiments, except where otherwise stated, were used 5 grms. of cotton, 5 per cent. of tannic acid, and 30 times the weight of water (of the weight of the cotton). The cotton was entered at 100°, and was allowed to cool with occasional stirring during three hours.

The following is a résumé of the results obtained:—

EFFECT OF TEMPERATURE.

1. The cotton was steeped cold for three hours.
2. The cotton was entered boiling and allowed to cool during three hours.
3. The cotton was steeped at 50° for three hours.
4. The cotton was steeped boiling for one hour.

* *Journ. Soc. Dyers and Col.*, 1892, p. 40.

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RESULTS.

	Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.
	Grm.	Grm.	Grm.
1	0·25	0·0363	0·2137
2	0·25	0·0513	0·1987
3	0·25	0·0082	0·2418
4	0·25	0·0025	0·2475

EFFECT OF CONCENTRATION.

Same conditions as above, but with varying amounts of water, viz :—

- | | |
|------------------|-------------------|
| 1. 75 cc. water. | 3. 300 cc. water. |
| 2. 150 „ | 4. 450 „ |

RESULTS.

	Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.
	Grm.	Grm.	Grm.
1	0·25	0·0663	0·1837
2	0·25	0·0513	0·1987
3	0·25	0·0288	0·2212
4	0·25	0·0238	0·2362

EFFECT OF TIME.

The original conditions were again adhered to, but the time was altered.

RESULTS.

Tannic Acid Taken.	Absorbed by Cotton.	Left in Solution.	Time.
Grm.	Grm.	Grm.	
0·25	0·0128	0·2372	30 min.
0·25	0·0168	0·2332	1 hr.
0·25	0·0490	0·2010	2 hrs.
0·25	0·0572	0·1928	4 hrs.
0·25	0·0609	0·1891	6 hrs.

The tannin is still being absorbed after six hours' immersion, and although the absorption is not in a direct ratio to the time of immersion, it is probable that the limit has not been reached in six hours.

CONSECUTIVE BATHS.

1. 5 grms. cotton were entered boiling and allowed to cool during $1\frac{1}{2}$ hours.
2. Same as No. 1. Wring out well, then enter a second 5 grms. at 100° and allow to cool again during $1\frac{1}{2}$ hours.
3. Same as No. 2, with a third lot of cotton.

RESULTS.

Tannin used.	Absorbed by 1st 5 Grms.	Absorbed by 2nd 5 Grms.	Absorbed by 3rd 5 Grms.	Left in Solution.
Grm.	Grm.	Grm.	Grm.	Grm.
0.25	0.0355	0.2145
0.25	0.0355	0.0195	...	0.1950
0.25	0.0355	0.0195	0.0103	0.1847

EFFECT OF WASHING OUT.

Enter boiling and allow to cool over night.

Absorbed by Cotton.	Left in Solution.
Grm.	Grm.
0.0612	0.1888

1. Steep in cold water (150 cc.) for one hour.
2. Steep in cold water (150 cc.) for three hours.
3. Steep in boiling water for one hour.
4. Enter into a solution of 10 per cent. tannic acid at boil and allow to cool during three hours.
5. As No. 4, using $2\frac{1}{2}$ per cent. tannic acid.

RESULTS.

	Left in Fibre.	Tannin extracted.
	Grm.	Grm.
1	0.0467	0.0147
2	0.0393	0.0221
3	None	0.0612
4	0.0198 + the 0.0612 absorbed	...
5	0.0007 lost	...

BLEACHED, UNBLEACHED, AND MERCERISED COTTON.

Same conditions as above.

Material.	Tannic Acid taken.	Absorbed.	Left in Solution.
	Grm.	Grm.	Grm.
Bleached Cotton, . .	0.25	0.0513	0.1987
Unbleached ,, . .	0.25	0.0568	0.1932
Mercerised ,, . .	0.25	0.1033	0.1467

The unbleached cotton was boiled previously for a short time with soap, to remove waxy and other impurities.

Precipitated Cellulose is capable of absorbing under similar conditions a much larger proportion of tannin than cotton yarn. By using 5 grms. of such cellulose, 150 cc. water, entering at 100° C., and allowing to cool during three hours, the following results were obtained :—

Tannic Acid taken.	Absorbed.	Left in Solution.
Grm.	Grm.	Grm.
0.25	0.1525	0.0975

The tannins play an important part in cotton dyeing, and are largely used for preparing cotton, so as to enable it to retain colouring matters permanently. Cotton when impregnated with a solution of magenta acquires a more or less intense bluish-red tint; the colour, however, can be easily removed by water. If the cotton had been previously impregnated with tannic acid, it attracts the dyestuff much more rapidly, and it is, under certain conditions, impossible to strip the colour by water. Frequently the purpose of preparing the vegetable fibres with tannin is not so much to fix the colouring matters themselves, although that is the ultimate aim, as to fix certain metallic oxides (notably the oxides of aluminium, copper, tin, and iron), in the form of insoluble tannates, which oxides fix the dyestuffs in the fibre by forming insoluble lakes with them during the subsequent dyeing process.

Tannic acid is the best "tannin" for the mordanting of cotton and linen, since it is the purest of all, and does not contain the natural impurities of the other materials, which are partly ineffective, partly injurious in mordanting and dyeing. It is especially more free from colouring matter than any other tannin. Tannic acid is almost exclusively used in the dyeing of light and brilliant shades, so that all the instructions given later will refer to pure commercial tannic acid. For dark shades extracts of gall-nuts, sumach, and myrabolans are largely employed, but the other materials find little application in cotton dyeing. Gall-nuts and decolourised sumach extracts give the best results next

to tannic acid, the quantity used depending on the amount of tannic acid they contain—as a rule, about 5 to 10 times as much as pure tannic acid is required. Cotton is prepared with tannin in the loose state, in the yarn, and in the piece, after the material has passed through the required cleansing and, if necessary, bleaching operations. Loose cotton and cotton yarn are soaked for some time in more or less diluted solutions, whereas cotton pieces can also be impregnated with strong solutions by the padding method.

Steeping Method.—A bath is prepared with 2 to 5 per cent. tannic acid (of the weight of the material), and a sufficient quantity of water to work the material (20 to 30 times the weight of the material). For very dark shades 5 to 10 per cent. tannic acid is required. The bath is used hot or cold. Cotton does not extract much tannin from the solutions above 60° C; yet hot solutions are employed to saturate the material quicker with the liquor, and to drive out all the air from the fibre. The cotton is worked in this liquor for some time, and soaked for from 3 to 12 hours—over night—while the bath cools. Mixed goods are not mordanted at a high temperature. (See below.) The material being sufficiently saturated, the excess of liquor is removed mechanically, and a light washing with water follows.

Padding Method.—Cotton piece goods are mordanted with tannin in the padding machine or jigger, because this process works more rapidly. For dyeing with basic colours, the pieces are run through a warm solution of tannic acid (2 to 3° Tw.), pressed out between squeezing rollers, beamed, and left for 1 to 2 hours. For blacks and for some basic colours, like the dark blues, stronger tannin liquor is taken.

Mixed cotton goods, containing either wool or silk, are mordanted at the ordinary temperature, so that the cotton only may take up tannin, and not the wool or silk.

The tannin-baths can be used continuously. They are exhausted more completely by additions of common salt or other salts, or sulphuric acid, which diminish the solubility of the tannic acid in water. Steel and Grandage recommend the addition of 10 to 15 per cent. (of the weight of the tannin) common salt, 2 per cent. sal ammoniac, and 1½ per cent. borax.

Cotton and linen retain the absorbed tannin, even resisting a moderate washing: but by continued washing and soaping the tannin is stripped.

Tannic acid forms lakes with the basic colours, which are insoluble in pure water, but dissolve in an excess of tannin and in other acids. The tannic acids can be converted into various metallic salts, which are insoluble in tannic acid or in water, and which, when produced in the fibre, resist soaping very well. These insoluble salts possess the same property as tannic acid in the free state of forming lakes with the basic colours; but an excess of the salts has no dissolving action on the colour-lakes, and the products are very stable. There

are in this way produced in the fibre *triple compounds* of tannic acid a metallic oxide, and a basic colour, which are quite insoluble in water, and resist both washing and soaping extremely well; and they are also faster to light than the lakes of tannin and colouring matter which do not contain a metallic oxide.

Antimony holds the first place as a fixing agent of tannin in dyeing with the basic colours; it yields the fastest colours both in regard to soap and to light; very good results are obtained with tin, less good with zinc; aluminium salts are used in special cases, and those of iron are only employed for the production of dark shades. The dark colour of the iron tannate does not permit its application for light shades, but effects a saving of dyestuffs in dark colours; in such a case the tannate of iron plays the double part of mordant and ground colour. The exact methods of fixation will be given in the chapters on the dyestuffs and metallic mordants.

In the inverse case of tannin being the fixing agent for a metallic oxide, the latter being the mordant proper, the material is impregnated in exactly the same way with tannin as described above.

Application to Wool.—Wool has so slight an affinity for tannin that the tannins are seldom applied to wool. Solutions of tannins have a tendency to render the wool fibre harsh or “hask,” especially if used at high temperatures, and great care must be taken to avoid this fault in the dyeing of mixed fibres. Tannic acid prevents, to a certain extent, the fixation of other colouring matters on wool. It is noteworthy that chromed wool which has been boiled or steeped in solutions of tannin cannot be dyed black with logwood. The colours thus obtained are browns which are not fast to light. Tannic acid is sometimes added to the dye-bath in dyeing alizarin colours on wool to prevent them from rubbing.

Application to Silk.—The tannins are extensively employed in the preparation of silk, both to strengthen and to weight the fibre. It seems that the tannins act in a similar manner on the silk fibre as on the animal skin, in so far as both lose their endosmotic and exosmotic properties on being saturated with these bodies. Silk loses, on being mordanted with tannins, in a remarkable degree the property of absorbing ferric salts (not ferrous salts) on dyestuffs, but it regains this power if the tannin is transformed into an insoluble tannate.

For the production of light shades the silk is worked and soaked in a cold solution of tannic acid or an extract of gall-nuts prepared without heating; it takes up in this way from 12 to 15 per cent. of its own weight. The impregnation takes place after the dyeing, since the tannin would be decomposed to some extent by the hot soap employed in dyeing and the shade would be dulled. The colouring matter of tannin has, in any case, a deteriorating influence on light tints.

As full and dark shades are less sensitive they allow of mordanting being effected at elevated temperatures and with inferior (*i.e.*, more

strongly coloured) tannins, especially sumach and myrabolans; for black the divi-divi or cheaper chestnut extracts are largely employed. The preparation with tannin takes place at about 70° C., and the weight of the silk is thus increased by about 25 per cent. The greatest absorption takes place at incipient boiling, but the increase is not considerable above 70° C.

The silk which has been completely saturated with tannin can be made to take up fresh quantities of the same by a treatment with ferrous salts. The material is worked in a strong solution of pyrolignite of iron, and exposed to the air to oxidise the ferrous tannate thus formed. It is then able to absorb fresh quantities of tannin. Use is made of this method in black dyeing.

Silk which contains tannin in the free state cannot be treated with a ferric salt, because it has lost its endosmotic property, and the ferric salt would simply destroy the tannin by oxidation. The case is different if the silk is first impregnated with a ferric salt and then passed through tannin liquor; in this manner ferric tannate is formed and the endosmotic property preserved; the silk is thereby enabled to take up alternately fresh quantities of ferric salt and tannin. The operation is best executed at 40° to 50° C.; at higher temperatures, especially above 70° C., ferric oxide exerts too great an oxidising action on tannin.

Silk is "weighted" by this method in black-dyeing up to 200 per cent. of its own weight. In the description of the iron mordants particulars are given as to the treatment of silk with ferrous and ferric salts.

Tannin is also applied to silk which has been dyed with Prussian blue, for weighting purposes. In this case, however, catechu and gambier are generally used. Frequently tin crystals are added to the tannin to increase the weight of the silk.

Silk dyed with Prussian blue takes up large quantities of tannin, which may vary, however, according to the temperature. Below 50° C. the silk absorbs 10 to 12 per cent. tannin without the Prussian blue itself being affected. At a temperature between 50° and 70° C. the Prussian blue is partially reduced, according to Moyret, by a portion of the tannin; and the oxides thus formed combine again with tannin, producing an increase of 30 to 40 per cent. and even more of the weight of the silk. By the treatment with tannin the blue silk is rendered capable of resisting hot soaping without the Prussian blue being decomposed.

The addition of stannous chloride is used for heavy weighting only; for an increase of the weight of more than 20 to 30 per cent. after the blueing, 5 to 15 per cent. tin crystals are added to the tannin-baths, which are heated to 70° or 75° C.; the temperature must not be higher. The hanks of silk must be worked very close together in the tin-tannin-baths so as to exclude the air as much as possible; for the same reason

the vat should be well filled with liquor. The oxidising influence of the air causes the material in the bath to assume a cloudy yellowish appearance, but, on washing with water, the full colour is restored.

The working in the tannin-baths lasts at least one hour; the goods may also be left overnight in the bath without being injured. The tannin-baths are used continuously; the tin-tannin baths are allowed to settle, and the clear liquor is used afresh; the tin which is contained in the sediment may be recovered by the process described for tin.

The tanned silk is finally rinsed in water and soaped in boiling hot solution of oil soap (30 to 40 per cent. of the weight of the silk) for two hours; for the soaping an old logwood bath is used with advantage. The silk may, then, be brought back to the tannin-bath, or finished in alkaline and acid olive oil (softening and brightening).

BASES AND SALTS.

Potassium Hydroxide or Caustic Potash, KOH —*Potassium Hydrate.*—Potassium hydrate is a white crystalline mass which melts below red heat, and is volatile at higher temperatures. It dissolves in half its weight of water and is very hygroscopic and deliquescent; the solution is called caustic potash-lye. Caustic potash is also very soluble in alcohol.

Potassium hydroxide is the strongest of all bases and is monacid; it possesses strong caustic properties and a caustic taste, and attracts carbon dioxide from the air to form potassium carbonate. Potassium hydroxide is manufactured by decomposing potassium carbonate with lime. It is used in the arts and in the laboratory. Sodium hydroxide, however, which strongly resembles it, is used in most cases, being considerably cheaper.

Potassium Carbonate, K_2CO_3 —*Carbonate of Potash; Potash.*—Potassium carbonate is the chief constituent of the ashes of land-plants. In former times it was obtained exclusively by extracting these ashes with water; great quantities are now manufactured on the large scale from potassium chloride (mined in Stassfurt) by the Leblanc process. (See *Sodium Carbonate*).

Potassium carbonate is a white substance which absorbs moisture from the air and is deliquescent; it crystallises with $1\frac{1}{2}$ molecules of water of crystallisation, $\text{K}_2\text{CO}_3 + 1\frac{1}{2}\text{H}_2\text{O}$. The solution has a caustic taste and shows alkaline reaction. It combines with carbonic acid, forming *potassium bicarbonate* (KHCO_3), which dissolves in 3 to 4 parts of cold water, is not deliquescent, and has a neutral reaction. Potassium carbonate is used in various industries, especially in the manufacture of soft soaps and of fine glass ware. It is used to a small extent only by dyers—in the dyeing of certain direct cotton colours. In most cases sodium carbonate, which is very similar, is used, as it is much cheaper than the potassium salt.

Potassium Hypochlorite, K Cl O —*Eau de Javelle*; *Chloride of Potash*.—Potassium hypochlorite is known only in aqueous solution which is obtained by the action of chlorine gas on caustic or carbonate of potash solution, or by double decomposition of chloride of lime and potassium carbonate.



Eau de Javelle has a chlorine-like smell (similar to chloride of lime), and is a strong bleaching agent, the power of which is increased by the addition of some acid. (See *Chloride of Lime*, p. 214). It is used chiefly in the household for bleaching purposes.

Potassium Chlorate, K Cl O_3 —*Chlorate of Potash*.—Potassium chlorate is obtained by saturating caustic potash solution with chlorine gas; on the large scale a mixture of lime and potassium chloride is used.



Potassium chlorate crystallises in shining tables belonging to the monoclinic system. The crystals are not very soluble in cold water, 100 parts water dissolving 6 parts of the salt at 15°C ., and 60 parts at the boiling temperature. On being heated above its melting point (359°) potassium chlorate gives off oxygen. Chlorate of potash is a powerful and convenient oxidising agent. In dyeing and printing it is employed in the production of aniline black and some other colours (for instance manganese bronze), as also for the preparation of mordants.

Potassium Chromate and Bichromate (see *Chromium*).

Potassium Sulphocyanide or Thiocyanate, K C N S , crystallises in transparent prisms, which are deliquescent, and melt readily on heating. It is very soluble in water, and absorbs a great quantity of heat on dissolving. It is used as a reagent for ferric salts, and may be employed to neutralise acids which are liable to carry iron into the colours.

Potassium Ferrocyanide, $\text{K}_4 \text{ Fe}_2 (\text{C N})_{12} + 6 \text{ H}_2 \text{ O}$.—*Yellow Prussiate of Potash*.—This salt is prepared by heating iron and potash with nitrogenous substances (animal refuse, such as clippings of horn, hoof, leather, &c.). It forms lemon-yellow crystals, containing water of crystallisation, $\text{K}_4 \text{ Fe}_2 (\text{C N})_{12} + 6 \text{ H}_2 \text{ O}$. It has a sweet-bitter saline taste and is not poisonous. It dissolves in 4 parts of cold and 2 parts of hot water, and is insoluble in alcohol. The solution on being boiled becomes alkaline, evolving ammonia and hydrocyanic acid. (See *Prussian blue*.) The commercial product often contains considerable quantities of potassium sulphate. Potassium ferrocyanide is used for the production of Prussian blue and in aniline black-dyeing. It forms precipitates with some basic aniline dyestuffs, and may be employed as a mordant for these on cotton.

Potassium Ferricyanide, $\text{K}_3 \text{ Fe} (\text{C N})_6$.—*Red Prussiate of Potash*.—This salt is manufactured by treating the yellow prussiate with oxidising agents like chlorine. It crystallises in dark-red prisms

which contain no water of crystallisation. 100 parts of cold water dissolve about 35 parts, hot water twice as much of the salt. Potassium ferricyanide is an oxidising agent. It is used as a discharge in printing and in the production of Prussian blue.

Potassium Oxalate, $K_2C_2O_4 + H_2O$.—Forms rhombic crystals, which are soluble in 3 parts of cold water.

Acid Potassium Oxalate ($KHC_2O_4 + H_2O$)—*Binoxalate of Potash*.—It forms monoclinic crystals, soluble in about 25 parts cold water.

Binacid Potassium Oxalate, $KHC_2O_4, H_2C_2O_4 + 2H_2O$.—Occurs in triclinic crystals, which are soluble in about 50 parts of cold water.

Commercial binoxalate of potash, salt of sorrel, is a mixture of the two acid oxalates. It is sometimes used as a mild acidifying substance, also as a substitute for tartar.

Acid Potassium Tartrate, $C_4H_4O_4(OH)(OK)$ —*Cream of Tartar, Tartar, Argol*.—This salt is obtained from the deposit which forms on the bottom of the vessels in which the fermentation of wine proceeds. In the crude state it is called "argol"—red or white, according as it is obtained from red or white wine; the ordinary purified product is known as "tartar," while "cream of tartar" is nearly pure acid potassium tartrate. The pure salt forms rhombic crystals; the commercial product is sold as a powder.

Solubility of acid potassium tartrate, in 100 parts of water, at

10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Part. 0·40	Part. 0·57	Part. 0·90	Parts. 1·3	Parts. 1·8	Parts. 2·4	Parts. 3·2	Parts. 4·5	Parts. 5·7	Parts. 6·9

Tartar is used in very large quantities as an assistant in the mordanting of wool with salts of aluminium, chromium, iron, copper, and tin, and serves to improve the permanence, fulness, and brilliancy of the ultimate colour. This influence is probably due to a double decomposition of the tartrate and the mordanting salt, the mineral acid of the latter combining with the potassium of the tartrate and the metallic hydrate with tartaric acid; it is also possible that a double salt is formed. At all events, it seems that the mordanting salt is changed in such a way that the fibre takes it up more readily and a better result is obtained. By mordanting wool with pure tartrates of aluminium, &c. (see *Aluminium on Wool*), excellent results are obtained. If, moreover, the tartaric acid which has been absorbed by the fibre is not properly washed out, it will, no doubt, exert a less injurious effect in dyeing than sulphuric acid in the free state (*Hummel*). Sometimes, as, for instance, in mordanting with bichromate and tartar, the latter salt acts also as a reducing agent.

A number of preparations are in the market under the name of

substitute of tartar, superargol, &c. Some are simply acid sodium sulphate; others contain oxalates; while still others are tartar, which contains sufficient sulphuric acid to convert all the potassium into potassium sulphate. In so far as these preparations claim to replace tartar completely, most of them are a direct fraud, because they cannot produce the double decomposition between the mordanting salt and a tartrate; if it is intended to use them for acidifying only, well-known and analysed chemicals—such as tartaric or oxalic acid or sodium bisulphate—should be preferred to preparations of unknown composition and properties.

Sodium Hydroxide or Caustic Soda, NaOH —*Sodium Hydrate.*—Sodium hydroxide is a white brittle mass of 2·13 sp. gr.; it melts at a low red heat, and is volatilised at higher temperatures; it is hygroscopic and deliquescent; it is exceedingly soluble in water, and easily soluble in alcohol. The aqueous solution is called caustic soda-lye.

Sodium hydroxide is a very strong monacid base, being inferior only to potassium hydroxide, and possesses strong caustic properties and a caustic taste. It absorbs carbon dioxide from the air to form carbonate of soda.

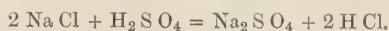
SPECIFIC GRAVITY OF CAUSTIC SODA AT 15° C., PERCENTAGES
OF Na_2O AND NaOH (*Schiff and Gerlach*).

Per cent. of the Solution.	Specific Gravity for Na_2O .	Specific Gravity for NaOH .	Per cent. of the Solution.	Specific Gravity for Na_2O .	Specific Gravity for NaOH .
1	1·015	1·012	31	1·438	1·343
2	1·020	1·023	32	1·450	1·351
3	1·043	1·035	33	1·462	1·363
4	1·058	1·046	34	1·475	1·374
5	1·074	1·059	35	1·488	1·384
6	1·089	1·070	36	1·500	1·395
7	1·104	1·081	37	1·515	1·405
8	1·119	1·092	38	1·530	1·415
9	1·132	1·103	39	1·543	1·426
10	1·145	1·115	40	1·558	1·437
11	1·160	1·126	41	1·570	1·447
12	1·175	1·137	42	1·583	1·456
13	1·190	1·148	43	1·597	1·468
14	1·203	1·159	44	1·610	1·478
15	1·219	1·170	45	1·623	1·488
16	1·233	1·181	46	1·637	1·499
17	1·245	1·192	47	1·650	1·508
18	1·258	1·202	48	1·663	1·519
19	1·270	1·213	49	1·678	1·529
20	1·285	1·225	50	1·690	1·540
21	1·300	1·236	51	1·705	1·550
22	1·315	1·247	52	1·719	1·560
23	1·329	1·258	53	1·730	1·570
24	1·341	1·269	54	1·745	1·580
25	1·355	1·279	55	1·760	1·591
26	1·369	1·290	56	1·770	1·601
27	1·381	1·300	57	1·785	1·611
28	1·395	1·310	58	1·800	1·622
29	1·410	1·321	59	1·815	1·633
30	1·422	1·332	60	1·830	1·643

Sodium hydroxide is prepared by decomposing sodium carbonate with lime, but in greater quantities from rock salt by a complicated process similar to the Le Blanc process for making sodium carbonate. For some years past almost pure caustic soda has been thus manufactured on a very large scale. The usual *brands of commerce are caustic soda* 48°, 60°, 70°, 74°, 76°, and 77°, each degree indicating 1 per cent. of sodium oxide (Na_2O); caustic soda, 77°, is almost chemically pure sodium hydroxide. The strength of a caustic soda is estimated by titration with standard acid (see *Analysis*), and the strength of a solution is roughly ascertained by the hydrometer (see Table). Of course, the latter method does not give good results in the case of the products containing carbonate, sulphate, chloride, &c., of sodium and other salts.

Sodium hydroxide is used in large quantities in the manufacture of soap, paper, and dyestuffs; as well as in bleaching, dyeing, and in many other industries.

Sodium Sulphate, Na_2SO_4 —*Glauber's Salt*, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$.—Sodium sulphate is produced by decomposing salt (sodium chloride) with sulphuric acid, hydrochloric acid also being formed.



Solubility of Sodium Sulphate (Anhydrous Salt, Na_2SO_4) in 100 parts of water at various temperatures.

0° C.	10° C.	15° C.	20° C.	25° C.	30° C.	33° C.	40° C.	103° C.
Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
5	9	13	19	28	40	50	49	42·6

Specific Gravity of Solutions of Anhydrous Sodium Sulphate (Na_2SO_4) at 15° C.

Specific Gravity.	Per Cent. Na_2SO_4 .	Specific Gravity.	Per Cent. Na_2SO_4 .	Specific Gravity.	Per Cent. Na_2SO_4 .
1·0091	1	1·0457	5	1·0832	9
1·0182	2	1·0550	6	1·0927	10
1·0274	3	1·0644	7	1·1025	11
1·0365	4	1·0737	8	1·1117 (saturated).	12

Most of the sodium sulphate which is manufactured is converted into soda; the greater part of the remainder is used for glassmaking. Sodium sulphate (without water of crystallisation) is obtained by calcination of crystallised Glauber's salt and by evaporating the solution above 33° C.; it is also called *calcined (anhydrous) Glauber's salt*. This salt occurs in rhombic crystals; it is readily soluble in water, but insoluble in alcohol. It attracts water from the atmosphere, thereby becoming moist; but it is not deliquescent. It dissolves at 21·5,

and at higher temperatures in water with evolution of heat; at $+3^{\circ}$ and below, with absorption of heat; for this reason it is sometimes mixed with ice or snow in order to produce artificial cold. It crystallises with 7 or 10 molecules of water from solutions below 33°C .

Glauber's Salt or *Glaubersalt*, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$, is obtained by crystallisation from solutions at temperatures below 33° , and forms large monoclinic crystals. It contains 44.1 per cent. anhydrous salt and 55.9 per cent. water. In the atmosphere it effloresces, and at 33° it loses the water of crystallisation. The term *sodium sulphate* is adopted in this work for the calcined Glaubersalt, and *Glaubersalt* for the compound, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$. They may be substituted for each other in the ratio of 11 calcined to 25 crystallised salt. The commercial products contain more or less sodium chloride, which, for most purposes, is not very objectionable. For the determination of the latter the quantity of chlorine present has to be estimated. The anhydrous salt may contain more sulphuric acid or less than is required by the formula Na_2SO_4 . The excess of either acid or alkali can be proved by the reaction on litmus paper, the colour of which is not affected by the normal salt.

Sodium sulphate is largely used by dyers, both in its crystallised and in its calcined form. It is employed in the finishing of cotton goods, and is found in most of the dyestuffs which are sold in the form of powders or pastes, occurring partly as an impurity resulting from the mode of manufacture, and partly as an addition for the purpose of reducing the colours to the usual standard of commerce. It is used by the dyer to regulate the dyeing operations in various directions.

If added in considerable quantities, sodium sulphate raises the boiling point of the dye-bath, and the increase of temperature thus obtained, although small, is of importance with some dyestuffs. Sodium sulphate also decreases the dissolving power of water for other substances, such as the dyestuffs. Hence it may exert a double effect—1. It ensures the more complete exhaustion of the dye-bath, since by decreasing the solubility of the colouring matters it forces them to pass more rapidly into the textile fibres. Such is the case with the direct cotton colours, which are attracted with greater power by the cotton fibre from saturated than from dilute solutions. 2. Sodium sulphate may cause the fibre to be dyed more evenly either by precipitating the dyestuff temporarily in a fine state of division (by "salting out"), or by preventing the same (if added in the form of a paste or dye-wood) from dissolving rapidly. It thereby causes the colouring matter to dissolve gradually, one part dissolving while another is withdrawn from the solution by the fibre, and not to rush on to the fibre.

Other neutral salts, such as sodium chloride, will exert the same effect as sodium sulphate in the preceding cases. In the following cases the action of sodium sulphate is based on the formation of the

acid salt, NaHSO_4 , but here sodium chloride would not be equivalent to the sulphate.

Sulphuric acid forms with sodium sulphate sodium bisulphate, and this compound has a less energetic acidifying action than the free sulphuric acid. The acid dyestuffs, therefore, are more slowly attracted by the fibre in the presence of Glaubersalt, and, consequently, they then dye more evenly; moreover, they are not retained by the surface so much, but penetrate deeper into the fibre, thus dyeing it better through. For this reason, most of the acid colours dye much better with comparatively small amounts of Glaubersalt in the dye-bath. In the case of it being desirable for shading to dye colours in an acid-bath which are not readily attracted by the fibre in the presence of an acid, sodium sulphate has a similar neutralising effect as in the former case, and enables the fibre to absorb such a colour (for instance, a basic colour) without preventing the dyeing of the acid dyestuff.

Finally, if a colour that has little dyeing power in the presence of free acid is to be prevented from dyeing too rapidly and, consequently, unevenly, sulphuric acid should first be added to the bath and thus be neutralised slowly by a gradual addition of sodium sulphate. In all these cases, of course, it makes little difference whether calcined or crystallised Glauber's salt is used, provided equivalent quantities are taken.

Acid Sodium Sulphate, NaHSO_4 —*Bisulphate of Soda*.—This salt, which is obtained by combining one equivalent of sodium sulphate and one equivalent of sulphuric acid, is frequently offered to the trade as *tartar substitute* and under similar fancy names. It crystallises both in the anhydrous state and with 1 molecule of water of crystallisation, and is very soluble in water. The diluted aqueous solution of the salt decomposes into sulphuric acid and sodium sulphate. Acid sodium sulphate is used as a mild acidifying agent, similar to a mixture of sulphuric acid and sodium sulphate as described above. Practical dyers state that the acid sulphate acts better than the mixture of the normal sulphate and sulphuric acid; this can be explained by the fact that the acid and normal salts do not readily combine in aqueous solutions, and that the acid remains in the free state, while it is liberated gradually when added in the form of the acid sulphate.

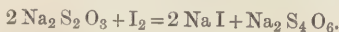
Sodium Sulphite, $\text{Na}_2\text{SO}_3 + 7\text{H}_2\text{O}$.—Sodium sulphite is obtained by the action of sulphur dioxide on a solution of sodium carbonate. It crystallises in monoclinic prisms which contain exactly 50 per cent. of water. It is fairly soluble in water, and not hygroscopic; when the solution is heated the anhydrous salt (Na_2SO_3) is separated. Sodium sulphite oxidises in the air and forms sodium sulphate.

The commercial product contains more or less sulphate as also carbonate; it should contain over 22 per cent. sulphur dioxide, which is estimated by the methods given for this compound.

Sodium Bisulphite, NaHSO_3 .—Sodium bisulphite is manufactured by saturating a hot solution of sodium carbonate with sulphur dioxide and allowing the product to crystallise. It forms white crystals which smell of sulphur dioxide, owing to liberation of that gas, and change to sodium sulphate by slow oxidation. A very similar product is *sodium metasulphite* ($\text{Na}_2\text{S}_2\text{O}_5$). Both are expensive products, and retain their original strength (about 62 and 66 per cent. respectively of SO_2) for a short time only. Generally the solution of sodium bisulphite is used (*bisulphite of soda*) which does not change in well closed wooden casks. As sold its specific gravity varies from 1.26 to 1.40 (52° to 80° Tw.). A solution heavier than 1.31 (62° Tw.) is liable to deposit crystals of bisulphite in very cold weather, which fact is not always noticed. A bisulphite of soda solution of the strength 52° to 62° Tw. should contain 20 to 23 per cent. sulphur dioxide (SO_2), be clear and nearly colourless, and smell of sulphur dioxide. Sodium bisulphite is used in the bleaching of wool and silk, for the preparation of the hydrosulphite vat, for rendering certain dyestuffs soluble (coerulein), as an antichlor, and for other purposes.

Sodium Thiosulphate or **Hyposulphite**, $\text{Na}_2\text{S}_2\text{O}_3 + 5\text{H}_2\text{O}$ —*Antichlor, Hyposulphite of Soda*.—Sodium thiosulphate is obtained from alkali waste. It is a very soluble and slightly deliquescent salt. Hydrochloric acid decomposes the aqueous solution, sulphur being separated in a finely divided state, and sulphur dioxide given off.

Sodium thiosulphate evinces strong reducing properties. It reacts with the halogens and transforms them into compounds with sodium; the reaction with iodine proceeds according to the equation—

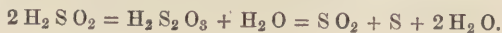


On this reaction is based the use of sodium thiosulphate in volumetric analysis. Chlorine reacts similarly to iodine with sodium thiosulphate. (See below.)

Commercial sodium thiosulphate is almost chemically pure. It is used sometimes as a mordant for wool, and finds application in the bleaching of textile fibres and paper pulp as an antichlor—*i.e.*, it transforms free chlorine into a non-oxidising compound, as indicated above.

Sodium Hyposulphite or **Hydrosulphite**, NaHSO_2 .—*Schuetzenberger's salt*.—This salt is not manufactured in the pure state, and is usually prepared by the consumers who use it for the reduction of indigo (*Hydrosulphite vat*).

Sulphurous acid is reduced by zinc or iron to *hydrosulphurous* or *hyposulphurous acid*, $2\text{H}_2\text{SO}_3 + \text{Zn} = \text{H}_2\text{SO}_2 + \text{ZnSO}_3 + \text{H}_2\text{O}$. Hydrosulphurous acid undergoes spontaneous decomposition; at first it yields sulphur, and forms thiosulphuric acid, and subsequently sulphur dioxide and sulphur are obtained—



Hydrosulphurous acid is a far more powerful reducing agent than sulphurous acid. The sodium salt is obtained by the reduction of sodium bisulphite (in strong solution) with zinc in the form of zinc-dust, or better, zinc-clippings, to avoid (too great an evolution of heat); the liquid must be kept cool—

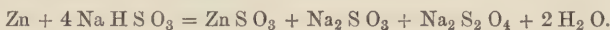


The zinc sodium sulphite separates in the form of crystals, while the sodium hydrosulphite remains in solution as long as the liquor is warm. The latter salt is not a stable compound; it readily takes up oxygen from the air to form sodium sulphite; and in the absence of air it soon decomposes, forming sodium thiosulphate—

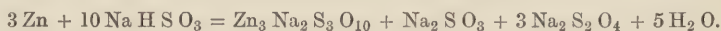


For this reason, only such quantities as are required for immediate use should be prepared.

According to Bernthsen,* the composition of sodium hyposulphite is not Na H S O_2 but $\text{Na}_2 \text{ S}_2 \text{ O}_4$. The first stage of the reaction takes place according to the equation—



On allowing to stand, it is found, however, that a larger proportion of bisulphite is reduced than would correspond to this equation. The complete reaction is shown by the following equation—



The more dilute the solution of bisulphite employed, the slower will the reaction be. Thus, whereas with a solution containing 0.5852 grm. Na H S O_3 in 100 cc., the maximum amount of hyposulphite was only formed in 265 hours, a solution containing 26.97 grms. in 100 cc. reached a maximum in $1\frac{1}{2}$ hours.

The practical preparation of hyposulphite is described under indigo and indophenol.

Sodium Chloride, Na Cl —*Common Salt, Rock Salt, Salt.*—Sodium chloride and its origin are well known. It forms crystals of the regular system, without water of crystallisation, melts at 776° , and is volatilised at a white heat. On being heated, the ordinary salt decrepitates, owing to mechanically enclosed moisture. The solubility of sodium chloride is nearly the same at different temperatures; 100 parts of water dissolve, according to Poggiale, at

0° C.	15° C.	25° C.	40° C.	60° C.	80° C.	100° C.
Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
35.5	35.9	36.1	36.6	37.3	38.2	39.2

and at the boiling point of the saturated solution ($109^\circ.7 \text{ C.}$), 40.35

* *Lieb. Ann.*, 208, p. 148.

parts. The specific gravity of salt solutions at 15° is, according to Gerlach :—

Per cent. Na Cl, .	5	10	15	20	25	26·4 (saturated).
Specific gravity, .	1·0362	1·0733	1·1114	1·1510	1·1923	1·2043

Commercial sodium chloride contains small quantities of sodium sulphate, calcium sulphate, and magnesium chloride, also some moisture.

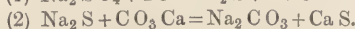
Sodium Nitrate, NaNO_3 —*Chili-* or *Soda-Saltpetre*.—Sodium nitrate is obtained in large quantities in the native state on the west coast of South America. It forms rhombohedric crystals, and is very soluble in water; it becomes moist in the air. It is used for the preparation of nitric acid, saltpetre, nitrites, as manure, &c.

Sodium Nitrite, NaNO_2 .—Sodium nitrite is manufactured by melting sodium nitrate with reducing substances, such as lead, iron, or calcium sulphite. It forms small crystals which are not deliquescent. The commercial article contains from 93 per cent. to 98 per cent. of NaNO_2 . Its valuation is effected with permanganate or with chemically pure sulphanilic acid.

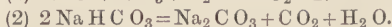
Sodium nitrite is used in the production of azocolours and some other dyestuffs, and has been recently introduced into the dye-house for the production of azocolours on the fibre.

Sodium Carbonate, Na_2CO_3 —*Soda Ash*; *Soda*; *Alkali*.—*Soda Crystals*, $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$; *Crystal Carbonate*, $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ (?).—Sodium carbonate is manufactured in immense quantities, chiefly by two methods :—

1. *The Le Blanc Process*.—Sodium sulphate as obtained from salt and sulphuric acid, is heated with coal and calcium carbonate; it is reduced thereby to sodium sulphide, and subsequently transformed into the carbonate.



2. *The Solvay or Ammonia Process*.—Salt in aqueous solution is decomposed by means of carbon dioxide and ammonia gas and converted into sodium bicarbonate and ammonium chloride; the former is heated until 1 molecule of carbon dioxide is driven off and sodium carbonate remains :—



Sodium carbonate is also obtained in the native state from some lakes (Salt Lake, Utah, U.S.A.). It is a white substance which melts at 814° C. It dissolves in water with evolution of heat, and crystallises with varying amounts of water. The well-known *soda crystals* have the composition $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$, and contain 37·1 per cent. sodium carbonate and 62·9 per cent. water. This compound forms monoclinic crystals.

Crystal carbonate (Gaskell, Deacon & Co.) is $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$, which formula corresponds to 14.5 per cent. water; the commercial product, however, contains about 18 per cent. water.

The solubility of sodium carbonate in water is greatest at $32^\circ.5$. The saturated solution boils at 105°C . According to Mulder, 100 parts of water at the temperatures given dissolve Na_2CO_3 in the following proportions:—

0°C .	5°C .	10°C .	15°C .	20°C .	30°C .	$32^\circ.5\text{C}$.	34°C . and 79°C	100°C .
Parts. 7.1	Parts. 9.5	Parts. 12.6	Parts. 16.5	Parts. 21.4	Parts. 38.1	Parts. 59	Parts. 46.2	Parts. 45.1

Sodium carbonate is stable in the air, has a caustic taste, and acts as a mild alkali. Most acids are neutralised by sodium carbonate, forming the corresponding sodium salts while carbon dioxide is driven off. With carbon dioxide it forms sodium bicarbonate. It strongly resembles potassium carbonate in its chemical properties.

Commercial sodium carbonate is sold under the name of "soda ash." It comes into the market in various strengths, chiefly 48° , 52° to 56° , and 58° , each degree indicating 1 per cent sodium oxide, Na_2O .

Soda ash (pure alkali), 58° , contains over 58 per cent. Na_2O or 98 to 99 per cent. pure sodium carbonate, and is pure enough for almost all technical purposes, especially all dyeing operations, and this is the article referred to under "soda ash" in other portions of this work. The other brands contain, in addition to sodium carbonate, chiefly harmless impurities, like sodium sulphate and chloride; also some caustic soda, which is objectionable for some applications, while in others its presence is a distinct advantage. A good product should be a white mass which dissolves in water without colour and without leaving much residue; it should be free from iron and from sulphides. (For analysis see Part XI.) The tables show the specific gravity of the solution.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE
AT 15°C .

Degrees Twaddle.	Percentage by weight.		Degrees Twaddle.	Percentage by weight.		Degrees Twaddle.	Percentage by weight.	
	Na_2CO_3 .	Na_2O .		Na_2CO_3 .	Na_2O .		Na_2CO_3 .	Na_2O .
1	0.47	0.28	11	5.23	3.06	21	9.90	5.79
2	0.95	0.56	12	5.71	3.34	22	10.37	6.06
3	1.42	0.84	13	6.17	3.61	23	10.83	6.33
4	1.90	1.11	14	6.64	3.88	24	11.30	6.61
5	2.38	1.39	15	7.10	4.16	25	11.76	6.88
6	2.85	1.67	16	7.57	4.42	26	12.23	7.15
7	3.33	1.95	17	8.04	4.70	27	12.70	7.42
8	3.80	2.22	18	8.51	4.97	28	13.16	7.70
9	4.28	2.50	19	8.97	5.24	29	13.63	7.97
10	4.76	2.78	20	9.43	5.52	30	14.09	8.24

Soda ash dissolves somewhat slowly on account of its forming hard lumps when in contact with water. Formerly the ash could not be bought in a state which was pure enough for many applications, and the more expensive crystals had to be used. Soda crystals dissolve readily, and are pure enough for all purposes; hence they are largely used—especially in the household—in spite of the increased expense for freight, &c. The commercial crystals are nearly pure $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$, except that they always contain some sodium sulphate. Crystal carbonate is nearly pure sodium carbonate, containing some water of crystallisation—about 18 per cent.—and possibly an excess of carbon dioxide.

SPECIFIC GRAVITIES OF SOLUTIONS OF SODIUM CARBONATE
AT 23° (*Schiff*).*

Specific Gravity.	Per cent. Na_2CO_3 + $10\text{H}_2\text{O}$.	Per cent. Na_2CO_3 .	Specific Gravity.	Per cent. Na_2CO_3 + $10\text{H}_2\text{O}$.	Per cent. Na_2CO_3 .
1.0038	1	0.370	1.1035	26	9.635
1.0076	2	0.741	1.1076	27	10.005
1.0114	3	1.112	1.1117	28	10.376
1.0153	4	1.482	1.1158	29	10.746
1.0192	5	1.853	1.1200	30	11.118
1.0231	6	2.223	1.1242	31	11.488
1.0270	7	2.594	1.1284	32	11.859
1.0309	8	2.965	1.1326	33	12.230
1.0348	9	3.335	1.1368	34	12.600
1.0388	10	3.706	1.1410	35	12.971
1.0428	11	4.076	1.1452	36	13.341
1.0468	12	4.447	1.1494	37	13.712
1.0508	13	4.817	1.1536	38	14.082
1.0548	14	5.188	1.1578	39	14.453
1.0588	15	5.558	1.1620	40	14.824
1.0628	16	5.929	1.1662	41	15.195
1.0668	17	6.299	1.1704	42	15.566
1.0708	18	6.670	1.1746	43	15.936
1.0748	19	7.041	1.1788	44	16.307
1.0789	20	7.412	1.1830	45	16.677
1.0830	21	7.782	1.1873	46	17.048
1.0871	22	8.153	1.1916	47	17.418
1.0912	23	8.523	1.1959	48	17.789
1.0953	24	8.894	1.2002	49	18.159
1.0994	25	9.264	1.2045	50	18.530

* The temperature of 23° has been selected, because strong liquors of sodium carbonate would separate crystals at 15°.

Sodium carbonate is, next to sulphuric acid, the most important of the chemical products. It is used by dyers for various purposes, and in large quantities in the bleaching of cotton goods.

Sodium Hypochlorite, NaClO —*Eau de Labarraque*, *Chloride of Soda*.—Sodium hypochlorite is analogous to potassium hypochlorite in composition. It has precisely similar properties, and is applied in the same way.

Sodium Chlorate, Na Cl O_3 .—Sodium chlorate has the same properties as potassium chlorate, except that it is much more soluble; consequently it is to be preferred when but little water can be used for dissolving the substance. It dissolves in its own weight of cold and half its weight of hot water. The price of sodium chlorate is also lower than that of potassium chlorate; the process of manufacture is similar.

Sodium Chromate and Bichromate (see *Chromium*).

Sodium Ferrocyanide, $\text{Na}_8 \text{Fe}_2 (\text{C N})_{12} + 24 \text{H}_2 \text{O}$, resembles the potassium salt, but contains more water of crystallisation.

Sodium Ferricyanide, $\text{Na}_6 \text{Fe}_2 (\text{C N})_{12} + \text{H}_2 \text{O}$, is also very similar to the potassium salt. It dissolves in 1.25 parts of boiling or in 5.3 parts of cold water, and is deliquescent in the atmosphere.

Sodium Arsenate, $\text{Na}_2 \text{H As O}_4 + 12 \text{H}_2 \text{O}$ —*Arsenate of Soda*—**Sodium Binarsenate**, $\text{Na H}_2 \text{As O}_4 + \text{H}_2 \text{O}$.—Arsenate of soda is obtained by evaporating a solution of arsenic in soda with the addition of sodium nitrate to dryness and heating the mass. The commercial product occurs either in crystals or in white masses, and has a greatly varying composition containing from 30 to 60 per cent. arsenic acid ($\text{As}_2 \text{O}_5$) and considerable quantities of common salt. It consists principally of the two above-named arsenates of sodium. A solution of the salt is also a commercial article.

Sodium arsenate is extensively used as a fixing agent for mordants, and as a substitute for cow-dung in the so-called operation of "dunging" or "cleansing." Its action consists in converting certain metallic mordants, especially aluminium and iron salts, into insoluble arsenates, and thus fixing them permanently. In calico printing sodium arsenate also prevents the loosely-adhering excess of mordant from being absorbed by those spots of the piece which should remain white, by making this excess insoluble, and therefore non-absorbable. It is especially used for the purpose of keeping the whites of print-goods clear. In yarn dyeing it affects the hands of the workmen owing to its poisonous properties. As it is so dangerous both to the workmen and to all who handle the dyed goods, while the neighbouring streams are liable to be contaminated with arsenical liquor, its use is objectionable; hence, in some countries, this has been prohibited. Minute quantities of arsenic remain in the finished goods, and may give rise to cases of poisoning, which, however, are very rare.

Sodium Phosphate, $\text{Na}_2 \text{H P O}_4 + 12 \text{H}_2 \text{O}$ —*Phosphate of Soda*.—This salt is found in commerce in the form of monoclinic crystals, which dissolve sparingly in cold water (1 in 25 at 10°C), but readily in hot water (1 in 1 at 100°C .) The salt effloresces in the air. The commercial product often contains sodium sulphate.

Sodium phosphate is used as a substitute for the arsenate in fixing aluminium and iron mordants. It does not act, however, so well as the arsenate, because aluminium phosphate is not insoluble under cer-

tain conditions. Liechti and Suida* state that sodium phosphate does not produce a precipitate in a large excess of aluminium sulphate; 2 equivalents of $\text{Al}_2(\text{SO}_4)_3$ are necessary to retain 1 equivalent AlPO_4 in solution. The high price of sodium phosphate also prevents it from being extensively used.

Sodium Tetrasilicate, $\text{Na}_2\text{Si}_4\text{O}_9$ —*Silicate of Soda*.—This compound is obtained by melting sand with soda ash and charcoal. It is met with in commerce under the name of *soluble glass*, either as a more or less coloured vitreous mass, or as a thick aqueous solution. The substance is very soluble in water, but it is not deliquescent in the air. The aqueous solution dissociates into acid and basic salts when diluted. Sodium silicate acts as a mild alkali; the commercial article sometimes contains an excess of caustic alkali. The aqueous solution is decomposed by carbon dioxide from the air, and should be kept in well-closed vessels.

Sodium silicate was first prepared by Fuchs for the preservation of "fresco-paintings," and is still used for this purpose. Textile goods, for example, stage decorations, light dresses, or curtains are impregnated with sodium silicate to prevent them from taking fire. Soap is "filled" with the substance to lower the cost of manufacture; and the addition should not be regarded entirely as an adulteration, since silicate of soda has, like soap, detergent properties. It is also used alone in bleaching, acting as a mild alkali. For certain dyestuffs (for instance, for aniline green) silicic acid in a finely-divided state serves as a mordant, and is produced on the fibre by saturating the goods with a solution of sodium silicate, and passing them through a weak acid. Sodium silicate serves also as a fixing agent for metallic mordants like the arsenate and phosphate, especially of iron and chromium. Aluminium salts treated with sodium silicate do not readily attract the colouring matter from the dye-bath, and do not yield such bright shades as when fixed by the arsenate. This is owing to the fact that silicic acid, being a very weak acid, does not readily combine with the aluminium hydroxide, so that the precipitation of the latter is more or less prevented by the basic silicates, which are generated by dissociation. (See above.) Besides, the commercial product contains an excess of caustic soda, which would cause the removal of the mordant from the fibre in the form of a soluble aluminate of sodium. Iron and chromium oxides, on the other hand, which are not soluble in the alkali, are well fixed by sodium silicate.

Sodium Borate, $\text{Na}_2\text{B}_2\text{O}_7 + 10\text{H}_2\text{O}$.—*Borax* forms monoclinic prisms; or, in the anhydrous state ($\text{Na}_2\text{B}_2\text{O}_7$), a white powder. The crystals dissolve in about twenty times their weight of cold, and half their weight of hot water.

Borax is used in the laundry, the laboratory, for the fluxing and

* *Journ. Soc. Chem. Ind.*, 1883, p. 537.

soldering of metals; also as a mild alkali in the dyeing of some direct cotton colours on cotton and of alkali blues on wool.

Sodium Acetate, $\text{Na C}_2\text{H}_3\text{O}_2 + 3\text{H}_2\text{O}$ —*Acetate of Soda*.—The salt forms crystals which lose their water of crystallisation in the air; they readily dissolve in water (1 part in 3.9 parts of water at 6° C.).

Sodium acetate is used to transform free mineral acids into their sodium salts, with liberation of acetic acid in cases where the former in the free state would prevent certain chemical reactions; or where they might tender the textile fibres, and where acetic acid would produce neither of these effects. For this reason sodium acetate is used in the preparation of diazocompounds in developing azocolours on the fibre.

S O A P.

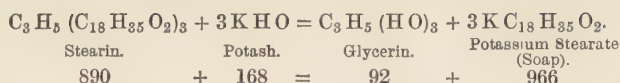
Vegetable and animal oils and fats consist for the most part of the glycerides of the higher fatty acids. Sperm and a few other similar oils are exceptions. They contain, in place of the radical of glycerin, solid monatomic alcohols, which are also combined with fatty acids.

Glycerides, when treated under suitable conditions with strong bases, are decomposed, glycerin is liberated, and salts of the fatty acids are formed. All such salts, in the widest sense, are "soaps."

In the ordinary sense, however, *soap* is understood to refer to the compounds formed by the action of fatty acids or their glycerides, upon the bases *potash* and *soda* only. These are soluble in water, all others (excepting ammonia soaps, which are not of much practical importance) are insoluble. Rosin or colophony, which contains pinic, sylvic, abietic, and other acids, also forms soaps with the alkalies. Rosin soap is not often used alone, but it enters largely into the composition of yellow household soaps. Excepting its use in bleaching calico for printing, soap containing resin is objectionable for general use in textile industries.

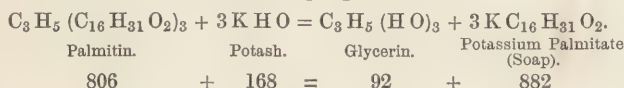
The most commonly occurring fatty acids in soaps are those obtained by the saponification of lard and tallow—viz., stearic, palmitic, and oleic acids. In addition to these, soaps frequently contain the following fatty acids:—Lauric acid, from cocoa-nut oil; brassic acid, from rape oil; linoleic acid, from linseed and other drying oils; and occasionally ricinoleic acid, from castor oil.

The fatty acids are monobasic acids, whereas glycerin, the radical of which is combined with the fatty acids in neutral oils and fats, plays the part of a tri-acid base. It is a tri-hydric alcohol. When oils and fats are boiled with potash or soda, saponification takes place, 3 molecules of alkali being required to displace 1 of glycerin. For example, stearin, which is glyceryl tristearate (the chief constituent of mutton fat), undergoes the following change when boiled with caustic potash:—



In this reaction 890 parts of stearin are decomposed by 168 parts of caustic potash, with the formation of 966 parts of anhydrous soap.

If palmitin or glyceryl tri-palmitate (the chief constituent of palm oil) be treated in like manner a similar reaction takes place; but, on account of the difference in molecular weights, the quantities are different, as shown by the following equation:—



In this case 168 parts of potash decompose only 806 parts of fat (palmitin), with the production of 882 parts of anhydrous soap. And according to the glycerides present in oils or fats, more or less potash is required to effect saponification of a given weight of fatty matter. This may be expressed in two ways; either by the amount of caustic potash required to saponify 100 parts of fatty matter, or the amount of oil or fat saponified by one equivalent of potash or soda. In the latter case the figure represents the "saponification equivalent" of the oil or fat. It is the quantity of oil or fat which is saponified by 56 parts of caustic potash, or 40 parts of caustic soda, and may be obtained by dividing the percentage of caustic potash required for saponification into 5600, or the percentage of caustic soda into 4000. In the case of fatty acids, the saponification equivalents are identical with their molecular weights (fatty acids being monobasic), whereas with the tri-glycerides or neutral fats and oils the saponification equivalents are one-third of their molecular weight.

The table on next page shows the saponification equivalents of the more important fatty acids, glycerides, natural oils and fats.

Natural oils from the same sources have not always exactly the same composition. They are not chemical compounds, but mixtures of several compounds—the glycerides. The majority of fixed oils on saponification yield from 95 to 96 per cent. of fatty acids, and about 10 per cent. of glycerin. Fats containing much lauric acid give rather different results. The following table contains a few examples of the theoretical proportions of fatty acid and glycerin, resulting from the saponification of pure tri-glycerides:—

				100 Parts of Glyceride yield	
				Fatty Acid.	Glycerin.
Laurin,	.	.	.	94·04	14·42
Palmitin,	.	.	.	95·28	11·41
Stearin,	.	.	.	95·73	10·34
Olein,	.	.	.	95·70	10·40
Brassein,	.	.	.	96·39	8·75
Linolein,	.	.	.	95·21	11·58
Ricinolein,	.	.	.	95·92	9·88

The increase in weight is due to what is termed "hydrolysis." On saponification the elements of water are taken up to form glycerin, and on decomposing the soap with a mineral acid water also takes part in the reaction to form the fatty acids.

FATTY BODY.					Percentage of Potash (K H O) for Saponification.	Saponification Equivalent.
Lauric Acid,	$C_{12} H_{24} O_2$,	.	.	.	28	200
Palmitic Acid,	$C_{16} H_{32} O_2$,	.	.	.	21·88	256
Stearic Acid,	$C_{18} H_{36} O_2$,	.	.	.	19·72	284
Oleic Acid,	$C_{18} H_{34} O_2$,	.	.	.	19·85	282
Brassic Acid,	$C_{22} H_{42} O_2$,	.	.	.	16·57	338
Linoleic Acid,	$C_{16} H_{28} O_2$,	.	.	.	22·22	252
Ricinoleic Acid,	$C_{18} H_{34} O_3$,	.	.	.	18·79	298
Laurin,	$C_3 H_5 (C_{12} H_{23} O_2)_3$,	.	.	.	26·38	212·7
Palmitin,	$C_3 H_5 (C_{16} H_{31} O_2)_3$,	.	.	.	20·88	268·7
Stearin,	$C_3 H_5 (C_{18} H_{35} O_2)_3$,	.	.	.	18·91	296·7
Olein,	$C_3 H_5 (C_{18} H_{33} O_2)_3$,	.	.	.	19·04	294·7
Brassein,	$C_3 H_5 (C_{22} H_{41} O_3)_3$,	.	.	.	16·00	350·7
Linolein,	$C_3 H_5 (C_{16} H_{27} O_2)_3$,	.	.	.	21·20	264·7
Ricinolein,	$C_3 H_5 (C_{18} H_{33} O_3)_3$,	.	.	.	18·06	310·7
Olive Oil,	19 to 19·5	287 to 295
Cotton-seed Oil,	19·1 to 19·7	284 to 293
Rape Oil,	17 to 17·6	318 to 330
Linseed Oil,	18·7 to 19·5	287 to 300
Palm Oil,	19·6 to 20·2	277 to 285
Cocoa-nut Oil,	24·6 to 26·8	208 to 228
Tallow,	19·3 to 19·8	283 to 290
Castor Oil,	17·6 to 18·1	310 to 319

The following table (pp. 200, 201), compiled principally from Allen's *Commercial Organic Analysis*, shows the origin and chief properties of the more important oils and fats (with oleic acid and resin) used in the manufacture of soap.

As a rule, the higher the solidification point of an oil or fat, the greater is the consistency of the soap made from it with the same alkali.

Soda forms much harder and firmer soaps than potash. In fact, all ordinary so-called *hard* soaps contain soda as the base, while *soft* soaps (often called "sweet" soaps) contain potash as the base. The hardest commercial soaps are those made with soda and fatty matter containing much stearic acid, such as tallow; and the softest are those made with potash and oils containing principally olein, linolein, or ricinolein. Potash soaps are highly deliquescent; according to Lant Carpenter, 100 parts of potassium oleate exposed to air absorb 162 parts of water, and 100 parts of potassium palmitate absorb 35 parts, whereas 100 parts of dry sodium stearate absorb only $7\frac{1}{2}$ parts. These

NAME OF OIL.	Source.	Chief components of oil.	Specific gravity.	Solidification point °C.	Saponification equivalent.	Lbs. of pure caustic potash required to saponify 100 lbs. of oil.	Lbs. of pure caustic soda required to saponify 100 lbs. of oil.	OTHER CHARACTERS, &c.
A. Of Animal Origin:								
BONE FAT, . . .	Bones of various animals.	Olein and palmitin.	234 to 293	19.1 to 19.7	13.6 to 14.1	Brownish colour; unpleasant smell. May contain calcium phosphate. Varies greatly in composition.
LARD,	From abdomen and other parts of the pig.	Olein, palmitin and stearin.	.860 to .863	27 to 44	286 to 292	19.2 to 19.6	13.7 to 14	
LARD OIL, . . .	Obtained by pressing lard.	Olein.	.915.	-4 to +10	290	19.3	13.8	Soluble in an equal weight of boiling alcohol. Gives a firm "elaiden."
TALLOW, . . .	From the ox and sheep.	Stearin, palmitin, and olein.	.860 to .863	33 to 48	283 to 290	19.3 to 19.8	13.8 to 14.2	Varies greatly in composition.
TALLOW OIL, . .	Obtained by pressing tallow.	Olein.	.916.	0 to 6	288 to 292	19.2 to 19.4	13.7 to 13.9	Much resembles lard oil.
WHALE OIL, . . .	Blubber of <i>Balaena mysticetus</i> and various allied species.	Olein (valerin).	.920 to .931	250 to 296	18.9 to 22.4	13.5 to 16	Yellow or brown colour; disagreeable fishy smell. Gives a pasty "elaiden."
B. Of Vegetable Origin:								
CASTOR OIL, . . .	Seeds of <i>Ricinus communis</i> .	Ricinolein.	.950 to .970	-18	310 to 319	17.6 to 18.1	12.6 to 13.1	Very viscous. Readily soluble in alcohol.
COCOA-NUT OIL, .	Nuts of <i>Cocos nucifera</i> and <i>butyrica</i> .	Laurin, palmitin, and stearin.	.868 to .874	16 to 18	208 to 228	24.6 to 26.8	17.6 to 19.2	Consistency of butter. Largely used for making "marine" soap.
COTTON-SEED OIL,	Seed of <i>Gossypium barbadense</i> and allied species.	Olein and stearin (linolein).	.922 to .930	1 to 4	284 to 293	19.1 to 19.7	13.6 to 14.1	Gives a pasty "elaiden." Fatty acids have a high melting point—viz., 38° C.

EARTH-NUT OIL, .	Nuts of <i>Arachis hypogaea</i> .	Olein, palmitin, arachidin	.916 to .920	- 5	289	19.3	13.8	Gives a firm "elaïden." Resembles olive oil, but contains glycerides of arachidic and hypogeic acids. Similar to linseed oil.
HEMPSEED OIL, .	Seed of <i>Cannabis sativa</i> .	Linolein.	.925 to .931	- 15 to - 28	290	19.3	13.8	Remains liquid when treated with nitrous acid. Similar to linseed oil.
LINSEED OIL, . .	Seed of <i>Linum usitatissimum</i> .	Linolein.	.930 to .937	- 20 to - 27	287 to 300	18.7 to 19.5	13.3 to 13.9	Gives a solid "elaïden" of a pale yellow colour.
NIGER-SEED OIL, .	Seed of <i>Guzotia oleifera</i> .	Linolein.	.924 to .928	Below - 9	289 to 295	18.9 to 19.4	13.5 to 13.8	Varies greatly in composition; often contains much free palmitic acid.
OLIVE OIL, . .	Fruit of <i>Olea Europea</i> .	Olein.	.914 to .917	- 6 to + 4	287 to 295	19 to 19.5	13.6 to 13.9	Gives a soft "elaïden."
PALM OIL, . . .	Fruit of <i>Avicaria elais</i> .	Palmitin and olein.	.857 to .859	20 to 36	277 to 285	19.6 to 20.2	14 to 14.4	Gives a pasty "elaïden."
RAPE-SEED OIL, .	Seed of <i>Brassica campestris</i> , &c.	Brassein.	.914 to .916	- 6 to - 10	318 to 330	17 to 17.6	12.2 to 12.6	Resembles tallow.
SESAMÉ OIL, . .	Seeds of <i>Sesamum indicum</i> .	Olein.	.921 to .924	- 5 to + 5	292 to 296	18.9 to 19.2	13.5 to 13.7	Varies greatly in composition; frequently contains glycerides as well as hydrocarbon oils.
SHEA BUTTER, .	Seeds of <i>Bassia parkii</i> .	Stearin and olein.	.859.	23 to 35	305	18.4	13.2	Used only in conjunction with other oils and fats, for yellow household soaps and sometimes for soft soaps.
OLEIC ACID or "OLEINE."	By pressing mixed fatty acids from tallow and palm oil (candles). Residue from distillation of crude turpentine.	Oleic acid.	.887 to .908	6 to 22	281 to 293	19.1 to 19.9	13.6 to 14.2	
RESIN or COLONY.		Abietic acid, &c.	1.04 to 1.10	135	290 to 330	17 to 19.3	12.2 to 13.8	

quantities, of course, are liable to vary according to the conditions of the atmosphere, but they show comparative results.

Some soaps, notably those made with cocoa-nut oil, have a remarkable property of retaining a very high percentage of water (70 to 80 per cent.) and still remaining fairly hard.

Soaps are insoluble in solutions of alkaline salts, and also in strong solutions of caustic alkali; hence, in the process of manufacture the potash or soda used must not be more than of a certain strength, otherwise the partially formed soap will be thrown out of solution. On the addition of common salt to a solution of soda soap, the latter separates out as a curdy mass and rises to the surface. This property is utilised on the large scale for separating the soap from excess of alkali and impurities in the "lye" employed. The glycerin liberated by the decomposition of the fatty matter also remains in the alkaline solution. The operation is usually termed "salting out." For the production of a pure neutral "curd" soap, the solution is run off, the soap dissolved in a fresh quantity of water, and the operation of salting out repeated.

When common salt is added to a solution of potash soap a double decomposition takes place, resulting in the production of a soda soap with formation of potassium chloride. In England, potash soaps are not "salted out;" hence, "soft" soaps made with neutral oils and fats invariably contain glycerin and usually excess of alkali. In some parts of the Continent where potassium chloride is abundant, this salt is used for the production of a neutral potash soap.

For details of manufacture, works such as W. Lant Carpenter's *Soap, Candles, &c.*, and Richardson and Watt's *Chemical Technology*, should be consulted. We shall only give here a brief outline. The methods employed for producing soap may be broadly classified as follows:—

I. By the direct saponification of fatty acids by caustic or carbonated alkalies.

II. By saponifying neutral oils and fats (glycerides) in the cold with exact quantities of strong solutions of caustic alkali.

III. By boiling oils and fats in large open vessels with comparatively weak solutions of caustic alkali, with subsequent concentration to a semi-solid mass.

IV. By boiling as in class 3 (but using caustic soda only), with subsequent "salting out" and elimination of the glycerin.

The first three processes are used for both potash and soda soaps. Soaps made according to methods I. and IV. contain no glycerin unless added direct. Those made by methods II. and III. retain the glycerin formed during saponification.

Method I.—The fatty acids employed are almost exclusively those obtained as a bye-product in the manufacture of stearic and palmitic acids for candles. The liquid portion known as "red oil" and "oleine" consists essentially of oleic acid, with small quantities of stearic and

palmitic acids. When prepared by the autoclave process, the product often contains more or less undecomposed glycerides as well as small quantities of hydrocarbon oils. If glycerides are present in notable proportions, it is best to saponify with caustic alkalies. Large quantities of soap, however, are made from "oleine" and potassium or sodium carbonate for washing raw wool, yarn, and cloth.

A solution of potash soap suitable for washing wool may be readily obtained by boiling 100 lbs. "oleine" and 25 to 30 lbs. of pure potassium carbonate (or an equivalent amount of commercial pearl ashes) with about 100 gallons of water in a large iron tank; 25 lbs. of potassium carbonate are required to produce a neutral soap, but for most kinds of work at least 30 lbs. may be used with advantage. A potash soap is admittedly superior to a soda soap for washing wool and woollen fabrics, but on account of cheapness soda is more frequently employed—especially for low-class goods. To produce a neutral soda soap with 100 lbs. of "oleine," about 19 lbs. of pure sodium carbonate are required, but in practice at least 25 lbs. are usually taken.

"Oleine," in addition to its direct use, is also largely employed in conjunction with other oils and fats for making soaps by the third process.

Method II.—In making soaps by the "cold process," the greatest care must be taken to employ the exact amount of caustic alkali required for saponification. The alkali used must also be pure and free from carbonate. This method is often employed for the manufacture of the cheaper kinds of toilet-soap, and of late years a considerable amount has been made for scouring purposes in the textile industries.

W. J. Menzies recommends the following quantities for making a good potash soap by the "cold process" for washing wool:—50 lbs. of Greenbank caustic potash are dissolved in 5 gallons of water and allowed to cool. The solution is then gradually poured into a vessel containing 200 lbs. of Gallipoli olive oil during constant stirring with a flat wooden stirrer about three inches broad. The stirring is continued until the oil and potash have become thoroughly mixed, when the vessel is covered and put in a warm place for a day or two. The combination between the oil and alkali commences a short time after mixing, and is accompanied by a considerable elevation of temperature.

The above quantities give an almost neutral soap. For anything but the finest work the amount of oil may be reduced to 180 lbs. It is preferable, however, to make a neutral soap and afterwards treat it with refined pearl ashes (potassium carbonate) in the proportion of 1 to 3 per cent.

In place of olive oil, cotton-seed oil, &c., or mixtures of these oils, may, of course, be used.

If it is desired to give the appearance of "figs" to the soap, a little tallow is used in place of a portion of the oil. A neutral hard soda

soap may be obtained in the following manner:—150 lbs. of tallow, palm oil, or cocoa-nut oil are melted and brought to a temperature not exceeding 40° C., and a solution of 20 lbs. of pure caustic soda dissolved in 75 lbs. of water at a temperature of about 22° C. gradually added during constant stirring. The mixture is then poured into a soap frame, covered up, and put in a warm place for a few days.

Method III.—Soft soaps are most usually made by boiling olive, cotton seed, linseed, rape seed, hemp seed, and other oils, or mixtures of these oils, with caustic potash lye. The oil is run into the “pan” to the extent of about one-fourth of its capacity, and the requisite amount of a solution of caustic potash (containing a little carbonate) of sp. gr. 1·065 to 1·08 (13° to 16° Tw.) added at the same time. The mass is boiled for some hours until saponification has taken place, the completion being determined by the appearance which small samples present when allowed to cool on glass plates. If more alkali is required, a solution of caustic potash, ranging from 1·12 to 1·2 sp. gr. (24° to 40° Tw.), is gradually and cautiously added, and the boiling continued. The direct steam (if used) is then turned off and a portion of the water evaporated by boiling with fire or “close” steam only. The finished soap is then run into casks while still hot.

“Hydrated” soda soaps are made in much the same manner as “soft” potash soaps, using an equivalent amount of caustic soda lye in place of caustic potash. The fatty matters used comprise tallow, palm oil, cocoa-nut oil, lard, oleic acid, castor oil, olive oil, &c. The amount of uncombined alkali in such soaps, although varying greatly, is usually much less than in soft potash soaps. Soaps of this class containing an excess of alkali are used largely for scouring purposes. Others which are neutral or contain an excess of fatty matter are extensively used as “softeners” for treating dyed cotton goods. For this purpose palm oil is the principal fatty matter employed.

Method IV.—Hard soaps made by open-pan boiling, where the glycerin is eliminated by “salting out,” are manufactured on an enormous scale. According to Lant Carpenter (*Soap and Candles*), probably 90 per cent. of the total soap produced in English-speaking countries is made in this way. The principal varieties are known as curd, mottled, and yellow. Almost all kinds of fatty matter are used, and for “yellow household” soaps resin is also largely employed, along with tallow, palm oil, and other fats.

Curd soaps should be free from resin. They are of great importance for milling and scouring dyed fabrics. It is generally considered that for these purposes, soap should be *perfectly* neutral, but this is a mistake. According to Thorp Whitaker,* who has had much experience with this subject, soap containing $\frac{1}{2}$ per cent. of free alkali in the form of carbonate, if properly used, does not injure the most delicate colours. On the other hand, inferior results would be obtained with a soap *absolutely* free from excess of alkali.

* *Journ. Soc. Dyers and Col.*, 1887, p. 41.

In many cases, after dyeing, the material (especially wool) contains a considerable amount of free acid, and if a perfectly neutral soap were subsequently used, a portion would be decomposed and free fatty acids deposited on the fabric.

The following tables show the results of a few analyses made by Rawson of scouring, milling, and softening soaps :—

POTASH SOAPS FOR WASHING RAW WOOL, &c.

In 100 Parts.	Made from Olive and Cotton-seed Oils.	Made from Olive Oil and Tallow.	Made from Olive Oil.	Made from Cotton-seed Oil.	Source unknown.
Water,	42·20	37·10	48·75	41·78	45·95
Combined alkali (K_2O), . .	9·20	10·08	7·32	9·05	7·78
Fatty anhydrides,	43·78	47·50	38·37	43·82	40·36
Potassium hydrate, . . .	·45	·28	·22	·15	} 1·50
Potassium carbonate, . . .	·82	1·58	2·05	1·40	
Glycerin, &c. (by diff.), . .	3·55	3·46	3·29	3·80	4·41
Melting point of fatty acids, } °C., }	29°	31°	26°	37°	32°

SODA SOAPS.

	FOR MILLING CLOTH.			FOR SCOURING PURPOSES.		
	Made from Tallow.	Made from Tallow and Palm Oil.	Made from Tallow, Cotton-seed Oil, &c.	Made from Palm Oil, Whale Oil, &c.	Made from Olive Oil.	Made from Tallow, Cotton-seed Oil, &c.
Water,	26·73	29·53	23·25	25·38	29·56	18·55
Combined soda } (Na_2O), . . . }	7·98	7·78	8·57	7·31	7·07	7·98
Sodium carbonate, . .	·18	·26	·12	·75	·35	·42
Fatty acids, . . .	67·22	64·05	69·50	65·40	64·11	72·60
Melting point of } fatty acids, °C. }	44°	40°	38°	36°	23°	37°

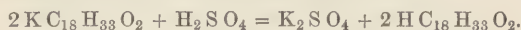
"SOFTENING SOAPS" (SODA).

MADE PRINCIPALLY FROM PALM OIL OR PALM OIL WITH OLEIC ACID.

	A.	B.	C.	D.	E.
Water,	66·80	64·40	32·50	28·05	67·50
Combined soda,	3·15	3·40	7·20	7·50	1·05
Fatty anhydrides,	25·95	30·50	54·35	59·15	7·25
Free fat,	1·05	·50	2·20	1·25	22·86
Sodium carbonate,	·15	·10	·25	·20	} 1·34
Glycerin, &c. (by diff.),	2·90	1·10	3·50	3·85	

Recovery of Fatty Matter from Waste Scouring Liquors.—

The waste liquors from the washing of raw wool contain, in addition to the soap and alkalies which have been used, the "yolk" of the wool. This yolk, which in different classes of wool varies greatly in quantity, is a complicated mixture of fatty and waxy bodies. It contains a considerable proportion of cholesterin and cholesteroid bodies which are unsaponifiable. On the addition of an acid to a solution of soap, the latter is decomposed with the formation of an alkaline salt and free fatty acids which rise to the surface. When sulphuric acid, for example, is added to a solution of potassium oleate (the principal constituent of an olive oil potash soap), free oleic acid rises to the surface and potassium sulphate remains in solution. The reaction takes place according to the following equation:—



On this principle the recovery of grease or fat from waste scouring liquors depends. The waste liquors are run into large tanks and thoroughly well mixed with a slight excess of sulphuric acid (chamber acid is usually employed for this purpose) by means of long rakes. After standing some hours the crude fatty matter rises to the surface. The under liquid, which contains alkaline sulphates, a little free sulphuric acid and glycerin (if present in the soap used) is run off and the magma of fatty matter collected and drained on filters made of coarse cocoa-nut matting. The separation of the fatty matter is accelerated by heating the mixture of soapy liquors and sulphuric acid in large wooden cisterns by means of steam, and this method is now generally adopted in modern works. After the excess of liquid has been drained away, the magma, which contains in addition to grease much dirt (organic and inorganic), bits of wool fibres, &c., is placed in canvas bags and introduced into a steam press. Steam is slowly admitted and a gradually increasing pressure applied. The fatty matters melt and flow out of the press along with water into a tank, from which the

oil is pumped into a purifying vessel. The cake which is left in the canvas bags still contains from 10 to 15 per cent. of grease, which, in some cases, is extracted by means of carbon disulphide.

The purification of the fatty matter merely consists in boiling it with a small quantity of dilute sulphuric acid. The acid solution is run off, and the oil transferred into casks. On cooling, it solidifies into a soft yellowish-brown mass, possessing a somewhat disagreeable odour. It is sold under such names as recovered grease, brown grease, Yorkshire fat, &c.

The composition of this recovered grease varies very greatly according to the kind of wool which has been scoured and the soap used in the operation. Recovered fatty matter from the washing of greasy wool contains a high percentage of wool-fat, much of which is unsaponifiable. If the wool contains but little grease, the recovered fat consists principally of the fatty acids derived from the soap, and contains only a small percentage of unsaponifiable matter. In some cases the wool is steeped in water only previous to scouring, by which means much of the "yolk" and potash salts are removed. When this is done, the soapy liquors give a less yield of recovered fat, but it is of superior quality. The following figures show the percentage of saponifiable and unsaponifiable matter in a few samples of recovered grease from wool scouring:—

Unsaponifiable, . . .	25·5	35	42·5	8·5	15·6
Saponifiable, . . .	74·5	65	57·5	91·5	84·4

When large quantities of alkaline carbonates are used in scouring, the value of the recovered fat may be less than the cost of production. The extent to which waste scouring liquors vary in composition is shown by the following partial analyses. All the four samples were obtained from the washing of raw wool:—

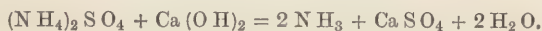
In 100 Parts.	1.	2.	3.	4.
Water,	99·38	97·10	96·50	97·80
Mineral matter, . . .	·15	1·05	1·30	·60
Oil or grease,	·27	1·20	1·52	1·36
Other organic matter (by diff.),	·20	·65	·68	·24
	100·00	100·00	100·00	100·00
Lbs. of pure sulphuric acid } required to neutralise 1,000 } gallons,	7	14	44	22
Lbs. of recovered fat per 1,000 } gallons,	27	120	152	136

According to G. H. Hurst,* recovered fat usually contains hydrocarbon oil as a normal constituent, but, unless mineral oils have been purposely or accidentally added, this is extremely unlikely. When the grease is distilled, as it is for many purposes, the product will contain hydrocarbon oils, formed by the partial decomposition of fatty acids.

After wool has been washed it is treated with a certain amount of oil (usually Gallipoli olive oil) to facilitate the carding operation. The wool, in the form of sliver, is subsequently washed with soap in what is known as a back-washing machine. In most works the waste "suds" from this operation are mixed with the waste liquors obtained in washing the raw wool. It is far preferable, however, to treat the waste liquor from the back-washing machines separately, since the recovered fatty matter, containing but very little unsaponifiable matter is much more valuable than the common brown grease.

The waste liquors from yarn scouring (especially worsted yarn) also yield a superior quality of recovered fat, consisting, as a rule, only of the fatty acids derived from the soap and vegetable oils.

Ammonia, NH_3 —Ammonium Hydroxide, NH_4OH —*Liquor Ammoniac.*—Ammonia is produced by heating ammonium sulphate with lime—



The solution is obtained by distillation of ammonia liquor from gas works.

Ammonia (NH_3) is a colourless gas of a most pungent and peculiar smell, by means of which it can be readily recognised. It is exceedingly soluble in water, 1 volume of water dissolving, at $15^\circ C.$, 730 volumes of ammonia; it is also very soluble in alcohol. The gas is driven out of both liquids by heat, and in open vessels it slowly escapes into the surrounding atmosphere. Ammonia can easily be liquefied by pressure, and the liquid is sold in a nearly pure state in iron cylinders under the name of "anhydrous ammonia." When liquefied ammonia evaporates under reduced pressure, it absorbs heat, and is, on this account, largely used in the manufacture of artificial ice.

The colourless liquid known under the name of *ammonia* is a solution of ammonia gas in water, and is supposed to contain the hydroxide, NH_4OH . The liquor has a specific gravity of about 0.88—*i.e.*, it is lighter than water, and the solution is lighter the more ammonia it contains. (See following table.)

Ammonia, both in the gaseous state and in solution, evinces very strong basic properties; it turns red litmus blue, and neutralises even the strongest acids, forming salts with them, which show a remarkable resemblance to the salts of potassium and sodium. The salts of ammonium contain the monovalent radical ammonium, NH_4 ; and the

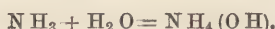
* *Journ. Soc. Chem. Ind.*, 1889, p. 90.

SPECIFIC GRAVITY OF LIQUOR OF AMMONIA AT 15° C. (*Langé and Wiernik*).

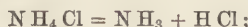
Specific Gravity at 15°.	Per cent. N H ₃ .	1 Litre contains grms. N H ₃ .*	Correction of the Specific Gravity for ± 1° C.	Specific Gravity at 15°.	Per cent. N H ₃ .	1 Litre contains grms. N H ₃ .	Correction of the Specific Gravity for ± 1° C.	Specific Gravity at 15°.	Per cent. N H ₃ .	1 Litre contains grms. N H ₃ .	Correction of the Specific Gravity for ± 1° C.
1.000	0.00	0.0	0.00018	0.960	9.91	95.1	0.00029	0.920	21.75	200.1	0.00047
0.998	0.45	4.5	0.00018	0.958	10.47	100.3	0.00030	0.918	22.39	205.6	0.00048
0.996	0.91	9.1	0.00019	0.956	11.03	105.4	0.00031	0.916	23.03	210.9	0.00049
0.994	1.37	13.6	0.00019	0.954	11.60	110.7	0.00032	0.914	23.68	216.3	0.00050
0.992	1.84	18.2	0.00020	0.952	12.17	115.9	0.00033	0.912	24.33	221.9	0.00051
0.990	2.31	22.9	0.00020	0.950	12.74	121.0	0.00034	0.910	24.99	227.4	0.00052
0.988	2.80	27.7	0.00021	0.948	13.31	126.2	0.00035	0.908	25.65	232.9	0.00053
0.986	3.30	32.5	0.00021	0.946	13.88	131.3	0.00036	0.906	26.31	238.3	0.00054
0.984	3.80	37.4	0.00022	0.944	14.46	136.5	0.00037	0.904	26.98	243.9	0.00055
0.982	4.30	42.2	0.00022	0.942	15.04	141.7	0.00038	0.902	27.65	249.4	0.00056
0.980	4.80	47.0	0.00023	0.940	15.63	146.9	0.00039	0.900	28.33	255.0	0.00057
0.978	5.30	51.8	0.00023	0.938	16.22	152.1	0.00040	0.898	29.01	260.5	0.00058
0.976	5.80	56.6	0.00024	0.936	16.82	157.4	0.00041	0.896	29.69	266.0	0.00059
0.974	6.30	61.4	0.00024	0.934	17.42	162.7	0.00041	0.894	30.37	271.5	0.00060
0.972	6.80	66.1	0.00025	0.932	18.03	168.1	0.00042	0.892	31.05	277.0	0.00060
0.970	7.31	70.9	0.00025	0.930	18.64	173.4	0.00042	0.890	31.75	282.6	0.00061
0.968	7.82	75.7	0.00026	0.928	19.25	178.6	0.00043	0.888	32.50	288.6	0.00062
0.966	8.33	80.5	0.00026	0.926	19.87	184.2	0.00044	0.886	33.25	294.6	0.00063
0.964	8.84	85.2	0.00027	0.924	20.49	189.3	0.00045	0.884	34.10	301.4	0.00064
0.962	9.35	89.9	0.00028	0.922	21.12	194.7	0.00046	0.882	34.95	308.3	0.00065

* The number of pounds of N H₃ per gallon is found by dividing by 100 the number in the third column (grammes of N H₃ per litre).

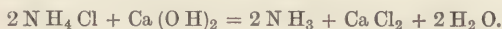
corresponding hydroxide, $\text{N H}_4 (\text{O H})$, probably exists in the solution of the gas—



Many salts of ammonia dissociate into the component acid and gaseous ammonia when strongly heated—



and when their solutions are heated with soluble bases, ammonia is driven off, while the base combines with the acid—



The same reaction takes place between the dry substances. (See above.)

Ammonia is always present in the atmosphere in minute quantities, being produced by electricity, by the evaporation of water into the air, by the decomposition of vegetable and animal nitrogenous matter, and by many other processes. Hence the air has a slightly alkaline reaction unless there is an excess of gaseous acids, especially sulphurous acid. While the atmosphere of the great cities is usually acid from sulphuric and sulphurous acids, the country air is generally alkaline.

Ammonia is employed for the purpose of neutralising acids in many industries (ammonia-soda, dyestuffs, &c.). By dyers it is used when a milder alkali than caustic soda is wanted; or where its volatility allows of the ready removal of an excess of the alkali, as, for instance, in neutralising Turkey-red oil. It is also used as a fixing agent for some metallic mordants—*e.g.*, lead salts and basic iron salts.

Putrid urine and dung are used in scouring and in certain operations in dyeing and printing, owing to the presence of ammonia in these substances.

Ammonium Chloride, $\text{N H}_4 \text{Cl}$ —*Sal Ammoniac*.—This salt occurs as a tough fibrous mass, or crystallises in arborescent forms of the regular system. It is very soluble in water; and when heated it volatilises completely without melting. In ancient times it was made by the burning of camel's dung in the oasis of Jupiter Ammon, hence the names *sal ammoniac* and *ammonia*. At the present time it is produced from ammoniacal gas liquor or ammonium sulphate.

Ammonium chloride is used for the fixation of aluminate of soda on the cotton fibre, in aniline black dyeing, &c.

Ammonium Carbonate, $(\text{N H}_4) \text{H CO}_3 + \text{CO} (\text{N H}_2) (\text{O N H}_4)$ —*Sal volatile; Salt of Hartshorn*.—This salt is formed by the putrefaction of nitrogenous substances like urine. In former times it was obtained by the destructive distillation of hide clippings, bones, or horn, hence the name salt of hartshorn (and spirit of hartshorn for ammonia-water). At present it is produced by heating ammonium sulphate with chalk.

Ammonium carbonate forms a white semi-transparent fibrous mass

which is readily soluble in water. It smells of ammonia, and absorbs from the atmosphere, moisture and carbonic acid, forming *ammonium bicarbonate*, $(\text{N H}_4) \text{H C O}_3$. Ammonium carbonate consists of this ammonium bicarbonate and *ammonium carbamate*, the ammonium salt of *carbamic acid*, $\text{CO} \begin{Bmatrix} \text{N H}_2 \\ \text{O H} \end{Bmatrix}$. When the salt is dissolved in water the

ammonium carbamate is changed into the *normal ammonium carbonate*, $(\text{N H}_4)_2 \text{C O}_3$, which is also known in the free state.

Commercial ammonium carbonate is used as a fixing agent for aluminium mordants in place of urine.

Urine is secreted by the kidneys from the arterial blood; it contains in solution a part of the nitrogenous waste of the animal organism in the form of *urea* $(\text{C O} \begin{Bmatrix} \text{N H}_2 \\ \text{N H}_2 \end{Bmatrix})$ and *uric acid* $(\text{C}_5 \text{H}_4 \text{N}_4 \text{O}_3)$. By putrefaction or fermentation the urea is converted into ammonium carbonate (as indicated by the smell of putrid urine).



The action of urine is chiefly due to this ammonium carbonate, which has a mild alkaline character. However, the fatty and albuminous substances, together with the small amount of ammonium phosphate [found in urine, may exert some influence. At present urine is not used to so large an extent as formerly, because substitutes have been found which are more regular in composition and pleasanter to work with, especially ammonia and carbonate of ammonium. The human urine only is used. It is employed in washing wool, in preparing some colouring matters, as orchil and cudbear, in the preparation of indigo-vats, and as a fixing agent of aluminium mordants.

Cow-dung.—Under this name are generally comprised the various kinds of dung, such as sheep's dung, &c. Dung contains a mixture of phosphates, carbonates, silicates, sulphates, and chlorides of calcium, potassium, sodium and ammonium, and other salts, albuminoid compounds, fatty acids, fibrous matter, and various other substances. When fresh it never has an acid reaction, and rarely a basic one. It is principally employed in so fixing the mordants on cotton piece goods prior to these being dyed, that the white parts shall remain clear. The action of cow-dung has not been completely explained; the phosphates, silicates, and carbonates, doubtless exert a fixing action, but the organic substances are not altogether inert. It is known that the latter are capable of forming precipitates with metallic oxides—*e.g.*, with red liquor; while they also act mechanically by absorbing the loosely adhering mordants and removing them completely from the fibre, so as to prevent them from spoiling the white of [printed goods. It is asserted that cow-dung gives better results than any substitute, such as the arsenates, phosphates, silicates, or carbonates; while it seems to act more slowly and evenly.

The dunging bath is principally formed of cow- or sheep-dung, and should not contain too much straw or iron; before being used it is often allowed to stand for some days with addition of some caustic soda, and subsequently diluted with 50 to 60 times its volume of water; the temperature of the dunging bath should be 50° to 65° .

Ammonium Acetate, $(\text{N H}_4) \text{C}_2 \text{H}_3 \text{O}_2$, forms crystals which are exceedingly soluble in water, but not deliquescent in the air. The dry salt is decomposed when heated. Recently the salt has been recommended as an addition to the dye-bath in the dyeing of woollen goods with alizarins.

Ammonium Sulphocyanide or **Thiocyanate**, $(\text{N H}_4) \text{C N S}$, crystallises in colourless laminae. It is very soluble in water and in alcohol, and absorbs heat on dissolving. It may be used for neutralising acids, which, by dissolving iron, are liable to transfer it to the colour.

Calcium Oxide, Ca O —*Quicklime*; *Burnt Lime*.—Calcium oxide is prepared by subjecting calcium carbonate (marble, limestone, oyster shells, &c.), to a bright red heat, $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$. The purest product is obtained from marble. Calcium oxide is a white, amorphous, porous mass of 3.08 sp. gr., which cannot be melted. It attracts moisture with great avidity, and with evolution of heat. It also absorbs carbonic acid from the air.

Calcium Hydroxide, $\text{Ca}(\text{OH})_2$ —*Calcium Hydrate*; *Slaked Lime*.—Calcium hydroxide is formed by the action of water on calcium oxide, $\text{CaO} + \text{H}_2\text{O} = \text{CaO}_2\text{H}_2$; or, as it is commonly called, “slaking” of lime, which is best effected by first moistening the quicklime with small quantities of hot water until the mass becomes very hot and begins to break up, and then adding more cold water. If the raw material contained clay, and has been heated too strongly, the quicklime does not slake well, and yields no good caustic lime. Calcium hydroxide forms a white powder of 2.01 sp. gr., which dissolves in 730 parts of water at 15° , and is less soluble at higher temperatures. The solution is called *lime water*.

Water containing calcium bicarbonate or organic substances is not well suited for making lime water, as the lime will soon be covered with insoluble substances, and be dissolved but slowly by the water. Lime water containing undissolved slaked lime, so as to appear milky, is known as *milk of lime*.

Calcium hydroxide is decomposed at a red heat into calcium oxide and water. It is a strong diacid base, turns red litmus blue, and absorbs with avidity carbon dioxide from the air, forming insoluble calcium carbonate, and rendering the liquid turbid. Calcium hydroxide is precipitated from the aqueous solution of calcium salts, if they are not too dilute, by caustic potash or caustic soda; in no case by ammonia. Hence strong solutions of potassium or sodium carbonate cannot be causticised with lime. In various chemical industries

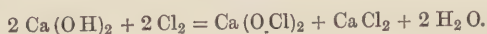
calcium hydrate is an important material—*e.g.*, in the manufacture of chloride of lime, caustic soda, &c. By bleachers and dyers it is used as a cheap alkali for bleaching cotton, as a fixing agent of iron mordants, in the preparation of the indigo-vat, &c. When solid (*i.e.*, lumpy) lime has been long in contact with cotton, it is liable to tender the fibre, and to cause uneven dyeing.

a ciumSulphate, CaSO_4 .—Calcium sulphate can hardly be said to belong to the class of dyers' materials; but it is certainly a very important substance in dyeing, because it is usually present in water, and is the chief substance which gives rise to the *permanent hardness of water*. It occurs crystallised in nature as anhydrite, CaSO_4 , and, combined with water, as gypsum and alabaster, $\text{CaSO}_4 + 2\text{H}_2\text{O}$. Calcium sulphate is soluble in about 400 parts of cold water. Gypsum when moderately heated loses its water, forming the so-called plaster of Paris. This takes up 2 molecules of water again when moistened, and forms a solid mass. Artificially prepared calcium sulphate or "annaline" is used by paper manufacturers.

Calcium Chloride, CaCl_2 , is formed by the action of hydrochloric acid on lime or chalk; and is obtained as a bye-product in many chemical processes—*e.g.*, in the manufacture of ammonia soda.

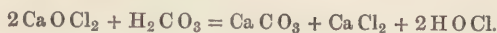
Calcium chloride is an extremely soluble and deliquescent substance, which is found in commerce as a white porous or as a solid dense mass; it also forms crystals with 6 equivalents of water. 100 parts of water dissolve 63 parts of calcium chloride at 10°C ., 120 at 40°C .; and 139 at 60°C .

Calcium Hypochlorite, $\text{Ca} \left\{ \begin{smallmatrix} \text{Cl} \\ \text{O Cl} \end{smallmatrix} \right\}$ or $\text{Ca}(\text{OCl})_2 + \text{CaCl}_2$ (?)—*Chloride of Lime* or *Bleaching Powder*.—Chloride of lime is produced by the action of chlorine gas on lime. The chlorine is passed over calcium hydroxide, which is spread in thin layers in lead chambers. Both the exact composition of the product and the chemistry of the process by which it is generated are still more or less obscure. The commercial product contains 35 to 39 per cent. available chlorine—*i.e.*, available in the form of hypochlorous acid. By the action of chlorine on moist lime, calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is formed according to the equation—



Chloride of lime is considered to be a similar compound. Bleaching powder, the commercial article, is a soft white powder which should not contain any lumps. It has the smell of hypochlorous acid and slowly becomes moist in the air. It is soluble in twenty times its own weight of water, but always leaves some insoluble residue. The solution on being heated gives off oxygen, while calcium chloride and calcium chlorate are formed. A solution containing an excess of caustic alkali is not readily decomposed by boiling. Carbonic acid

expels the hypochlorous acid; and in this way chloride of lime is decomposed by the atmosphere.



Hypochlorous acid subsequently decomposes, forming oxygen in the nascent state—



To the oxidising action of this oxygen is due the bleaching power of chloride of lime and of all hypochlorites (*Eau de Javelle*, &c.). The effect of all these compounds is increased if some acid is added to the solution of bleaching powder; only a very small amount of acid is required to start the reaction, fresh acid being generated by the process itself, so that it becomes continuous.



Recently (Engl. Patent, 1884, No. 11,333) the employment of formic and acetic acid, for this purpose, has been patented by G. Lunge.

Chloride of lime, when used for the bleaching of cotton and linen goods, is applied in the form of a perfectly clear very diluted solution, 1·003 to 1·007 sp. gr. ($\frac{1}{2}$ to $1\frac{1}{2}$ ° Tw.). If solid lumps of chloride of lime should occur in the solution they may settle on the fibre, so as to weaken it, or at least may give rise to uneven dyeing by forming oxycellulose. The solution should be prepared in the cold because chloride of lime is decomposed on boiling (see above).

The largest quantities of bleaching powder are consumed for the bleaching of cotton, flax, hemp, and materials for the manufacture of paper; while next in importance is its use as a disinfectant. It is also used largely as an oxidising agent in various chemical industries—*e.g.*, as a discharge in calico printing.

The preparation of solutions of bleaching powder is not a very simple nor an economical operation. Where the expense of carriage is not too great the liquor (bleaching liquor), made direct from milk of lime, is bought from the works by the consumers.

Other bleaching liquors, the active constituents of which are hypochlorites, are also used. The most important of these are the so-called *Eau de Javelle* and *Eau de Labarraque*. In addition may be mentioned the hypochlorites of magnesium, of zinc, and of aluminium; the last named is known as Wilson's bleaching liquor.

Calcium Carbonate, CaCO_3 —*Chalk, Carbonate of Lime*.—Calcium carbonate occurs widely diffused as chalk, limestone, coral, marble, calc-spar, and aragonite—in the amorphous and in various crystallised forms. It is almost insoluble in water (2 parts in 100,000 parts of cold or boiling water); but more soluble in water containing carbonic acid (88 parts in 10,000 parts of such water at 10°). When the carbonic acid is driven from the water by heat, the calcium carbonate

is precipitated. The hardness of natural waters, due to dissolved calcium carbonate, is known on this account as *temporary hardness*. Calcium carbonate has mild basic properties, and is readily decomposed by acids. It is used by chemical manufacturers to neutralise acid liquids, and by dyers as a mild alkali for neutralising acids for the fixing of mordants (Turkey-red dyeing, "chalking"), and for introducing into the dye-bath the amount of lime necessary for the dyeing with alizarin. For these purposes it should be light, soft, and almost completely soluble in diluted hydrochloric or acetic acid. It should not contain carbonates or hydroxides of the alkalies. The latter can be detected by the reaction of an aqueous extract on phenol phtaleïn, which must not be coloured thereby.

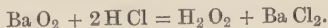
Calcium Sulphocyanide or Thiocyanate, $\text{Ca}(\text{CNS})_2$, crystallises with 3 equivalents of water, and is very soluble in water. The crude liquor, obtained from gas water, is used for the preparation of other sulphocyanides in textile printing.

Calcium Acetate, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$ —*Acetate of Lime*.—Calcium acetate is produced by neutralising acetic acid with lime. It crystallises with 1 equivalent of water, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$. It is very soluble in water, is precipitated from solution by alcohol, and, chemically, acts as a neutral salt, although it turns red litmus blue.

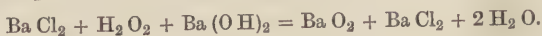
Calcium acetate occurs in two forms in commerce—*brown or grey acetate of lime*, the crude product obtained from pyroligneous acid; and *white acetate of lime*, a purer article. To obtain pure calcium acetate, free from iron, dyers prepare it for themselves by neutralising lime with acetic acid—about 7 parts of acetic acid (30 per cent. strength) to 1 of quicklime (CaO) are necessary; litmus paper does not show the point of neutralisation.

Calcium acetate is a mordant proper, since calcium is an integral constituent of the alizarin lakes, and it is introduced into the colour in the form of the acetate; it is also used in the preparation of other acetates which serve as mordants—*e.g.*, aluminium acetate; but its principal use is in the manufacture of acetic acid.

Barium Peroxide, BaO_2 .—Barium peroxide is produced when a current of oxygen is passed over gently-heated barium oxide. It forms a greyish-white porous mass, and dissolves in dilute acids, forming peroxide of hydrogen—



On the other hand, barium salts in alkaline solutions are converted by hydrogen peroxide into barium peroxide—



On being heated beyond 400°C ., barium peroxide is decomposed into oxygen and barium oxide. Barium peroxide is used for the preparation of hydrogen peroxide, and of pure oxygen.

Barium Sulphocyanide or Thiocyanate, $\text{Ba}(\text{CNS})_2$, crystallises

with 2 equivalents of water, and is very soluble and deliquescent. It is used for the preparation of sulphocyanides, which serve as mordants in textile printing.

Magnesium and its Compounds.—Magnesium sulphate is the only compound of magnesium which is largely used in dyeing, but as some others may become important, a short description may be given.

Magnesium, Mg, is a silver-white metal which does not rapidly oxidise in the air. It burns with a dazzling white light, which is extremely rich in chemically active rays. It forms a valuable substitute for sunlight in photography, and is used by dyers for matching-off colours when daylight is not available.

Magnesium Oxide or *Magnesia usta*, MgO , and **Magnesium Hydroxide**, Mg(OH)_2 , are white amorphous powders, almost insoluble in water. They are weak binacid bases, and are readily soluble in most acids. With the fatty acids, however, they form insoluble soaps.

Magnesium Sulphate, MgSO_4 , occurs in nature as *kieserite*, $\text{MgSO}_4 + \text{H}_2\text{O}$, and as *Epsom salt*, $\text{MgSO}_4 + 7\text{H}_2\text{O}$. The former is almost insoluble in water, the latter is very soluble in water (in 3 parts at 15°C). It is prepared on the large scale from kieserite and magnesite, and occurs in commerce in rhombic crystals or as a crystalline powder. Magnesium sulphate is used in medicine, in wool dyeing (for some basic colours), and in the finishing of cotton goods. If used for the latter purpose, it should not contain any magnesium chloride, as the latter is liable to generate hydrochloric acid in the free state at the temperature of the calender roller, and thus might tender the fibre.

Magnesium Chloride, MgCl_2 , is a very soluble and deliquescent substance. On being heated, it decomposes into *magnesium oxychloride*, MgCl(OH) , and hydrochloric acid. As mentioned above, it is liable to weaken the fibre under certain conditions. Water containing much magnesium chloride is not suitable for feeding steam boilers, because the acid which is set free corrodes the iron.

Magnesium Carbonate, MgCO_3 , is found native as magnesite. It is almost insoluble in pure water, but readily soluble in water containing ammonium salts or carbonic acid.

Magnesium Acetate, $\text{Mg(C}_2\text{H}_3\text{O}_2)_2$, crystallises with 4 equivalents of water. It is very soluble. It has recently been proposed as a mordant (compound mordants, H. Koechlin), and can be obtained by the double decomposition of magnesium sulphate and lead acetate, or by dissolving magnesium carbonate in acetic acid. In printing colours for calico, it plays the part of a powerful alkali.

ALUMINIUM, $\text{Al} = 27.1$.

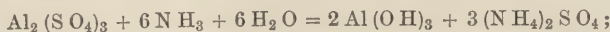
In the pure state, aluminium is a perfectly white metal, but as produced it has a bluish-white tinge; the specific gravity is 2.5, the

melting point about 700° C. Under all ordinary conditions it is not acted upon by air and moisture, sulphuretted hydrogen, ammonium sulphide, or cold acids, except hydrochloric acid. The non-corrodibility, however, depends upon the freedom of the metal from silicon, iron, and the commercial product is more or less easily attacked by chemical agents. Aluminium is readily corroded by alkaline solutions which form aluminates, by hydrochloric acid and chlorine, and is acted upon more or less by solutions of chlorides. Salts of aluminium are not poisonous.

Aluminium is a trivalent metal. The formulæ of aluminium compounds are usually written with 2 atoms of aluminium, like $\text{Al}_2(\text{O H})_6$ instead of $\text{Al}(\text{O H})_3$, and Al_2Cl_6 instead of AlCl_3 , because aluminium was supposed to be quadrivalent, and to play the part of a hexad in the combination of 2 atoms, like $\equiv\text{Al}-\text{Al}\equiv$ or Al_2^{VI} .

Aluminium Oxide, Al_2O_3 —Alumina.—Aluminium oxide occurs native as corundum, ruby, sapphire, and emery. It is prepared as an amorphous powder of 3.75 to 3.9 sp. gr. by heating aluminium hydroxide. When prepared by gentle heat it is readily soluble in acids; by the application of higher temperatures, however, it becomes insoluble in acids. All modifications of alumina become soluble in acids, when melted with caustic alkalis.

Aluminium Hydroxides, Aluminium Hydrate, Alumina.—The *Aluminium hydroxide*, $\text{Al}(\text{O H})_3$ or $\text{Al}_2(\text{O H})_6$, is formed when ammonia is added to the solution of an aluminium salt—



from cold solutions it is obtained as a gelatinous substance, from hot solutions as a white powder; the presence of organic substances like oxalic, tartaric, or citric acid or sugar may prevent the precipitation more or less. The dry mass on being heated is converted into the *aluminium hydroxide*, $\text{AlO}(\text{O H})$ or $\text{Al}_2\text{O}_2(\text{O H})_2$, and by continued heating into the oxide, Al_2O_3 . *Aluminium hydroxide*, $\text{Al}_2\text{O}(\text{O H})_4$, which is, like the preceding compounds, not soluble in water, is obtained by boiling the ordinary hydroxide, $\text{Al}(\text{O H})_3$, with water for 24 hours. Graham obtained by dialysis of aluminium hydroxide, which was dissolved in a solution of aluminium chloride, a *soluble hydroxide*, $\text{Al}(\text{O H})_3$. This substance coagulates on heating, as also on the addition of acids, bases, and salts; it is attracted by the textile fibres, and acts as a mordant. Another *soluble hydroxide*, $\text{Al}_2\text{O}(\text{O H})_4$, was prepared by Walter Crum* by heating a solution of aluminium acetate, which contained one part of aluminium, in 200 parts of water, for 24 hours in a closed vessel. This compound coagulates like Graham's hydroxide, but does not behave as a mordant.

Aluminium hydroxide acts both as a weak (triacid) base and as a very weak acid. It forms *aluminium salts* with acids, and *aluminates* with bases.

* *Liebig's Ann.*, 89, p. 168.

Aluminium hydroxide is also precipitated from the solutions of the aluminium salts by the hydroxides and carbonates of potassium and sodium; organic substances prevent the precipitation more or less. By an excess of caustic potash or soda the hydroxide is readily redissolved (with formation of the aluminates); ammonium salts, especially on boiling, prevent it to a great extent from redissolving. The hydroxide does not dissolve in ammonia except a great excess of caustic ammonia is applied, and when no considerable quantities of ammonium salts are present. An excess of the carbonates dissolves but very little of the hydroxide.

Caustic alkalies do not redissolve aluminium hydroxide if the precipitation has been effected in the presence of a magnesium salt (*Double Mordants* of Horace Koechlin). In mordanting with the acetates of alumina or chrome, acetate of magnesium (or calcium) is added to the dye-bath for fixing on cotton such colours as phloxin or xyloidine-scarlet. A method indicated by Koechlin for the dyeing of St. Denis red consists in working the fibre in a mixture of aluminium and magnesium salt, and then passing it through a solution of zincate of soda. The substitution of the latter for caustic soda, introduced by Weber of Winterthur, has the advantage of fixing an insoluble aluminate of zinc in the fibre; in this particular case a *triple mordant* is formed.*

Aluminium hydroxide, on being precipitated from solutions of aluminium salts, attracts many inorganic and organic substances which are in the same liquid, either in suspension or in solution, and is used on this account in clarifying drinking water, sugar solutions, &c. Many vegetable and artificial colouring matters are also attracted by aluminium hydroxide and precipitated from their solutions, forming "colour-lakes"; the liquid thereby becomes decolourised if enough aluminium hydroxide is used. The lake-forming action of the aluminium mordants when fixed on the fibre is precisely similar.

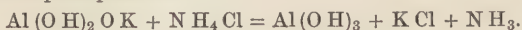
Aluminates.—Aluminium hydroxide possesses the character of a weak acid oxide, and forms with basic hydroxides salts which are called aluminates.

The aluminates are prepared by melting aluminium oxide with bases or with the corresponding carbonates. Potassium and sodium aluminates are also obtained by dissolving aluminium hydroxide in caustic potash and caustic soda. The aluminates which are produced in the dry way are derivatives of the aluminium hydroxide, AlO_2H —e.g., $\text{Ba}(\text{AlO}_2)_2$. A great many of these occur as minerals. Potassium aluminate is obtained in crystals from aqueous solutions, as $\text{Al}(\text{OH})_2(\text{OK})$, or $2\text{Al}(\text{OH})_2\text{OK} + \text{H}_2\text{O}$. Sodium aluminate has not been prepared in a crystalline form.

On the whole the acid character of aluminium hydroxide is less distinct than the basic. The solutions of aluminates are decomposed

* Prudhomme, *Journ. Soc. Dyers and Col.*, 1891, p. 133.

by all acids, even by carbonic acid; aluminium hydroxide is precipitated and a potassium or sodium salt remains in solution. In a similar way the solutions of aluminates are decomposed by ammonium salts; potash or soda, as the stronger bases, combine with the acid of the ammonium salt, whereas the liberated aluminium hydroxide does not combine with the ammonia and remains in the free state in the form of a gelatinous precipitate.



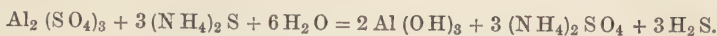
Use is made of this reaction in fixing the mordant.

Aluminate of Soda—*Alkaline Pink Mordant*.—This article is prepared by melting cryolite with lime or bauxite with soda ash. It can also be obtained by adding caustic soda to a strong solution of aluminium sulphate until the precipitate at first formed is redissolved, and no fresh precipitate is produced on addition of more caustic lye. A slight excess of alkali makes the solution more stable and is not injurious. If a small amount of caustic lye is used the precipitate redissolves also at first with formation of basic aluminium sulphate; on adding more alkali, however, a fresh precipitate is formed, until all sulphuric acid is neutralised by the caustic soda. Aluminate of soda occurs in commerce as a lumpy powder of a white, slightly greenish colour. It is readily soluble in water, but not deliquescent, and is decomposed by carbon dioxide in the presence of moisture. It is used as a mordant for alizarin red on cotton piece goods (see *Schlieper's process*), but cannot well be employed on cotton yarn on account of the caustic action it has on the hands of the workmen.

Aluminate of soda offers the great advantage that it does not carry iron into the ultimate colour, and that it is fixed on the fibre in a short time without ageing. It finds but limited employment, because it cannot be associated with acid mordants. The goods are simply impregnated with the aluminate, rapidly dried at an elevated temperature, and passed through a solution of ammonium chloride (10° Tw.) at 50° to 60° C. The aluminium is thus fixed in the form of aluminium hydroxide. The hydroxide is also fixed to some extent by mere exposure to the atmosphere. Other salts can be substituted for the ammonium chloride—*e.g.*, zinc sulphate, chloride, or acetate. It seems, however, that they do not offer any advantages over the ammonium salts. Aluminate of soda is not used as a mordant for wool or silk, because it is too alkaline for these fibres.

Aluminium Salts.—The salts which aluminium forms with acids are colourless. Most of the ordinary salts are readily soluble in water, and possess a sweet astringent taste, reddening blue litmus, and lose their acid if subjected to strong heat. The solutions of the normal aluminium salts are not decomposed by boiling or by dilution with water (in contrast with the basic salts). They are not changed by carbon dioxide or by sulphuretted hydrogen, neither a carbonate nor a sulphide being formed. On addition of ammonium sulphide no

sulphide is obtained; the sulphuretted hydrogen is simply liberated, and aluminium hydroxide formed:



The behaviour towards alkalis, &c., has been described with the hydroxide.

Sodium phosphate precipitates from the solutions of aluminium salts, *aluminium phosphate*, AlPO_4 .



The precipitate forms a voluminous white mass, which is soluble in caustic soda, but not in ammonia. It also dissolves in hydrochloric or nitric acid, but not in acetic acid. Citric acid prevents the formation of the precipitate, but not tartaric acid or sugar. Aluminium phosphate is soluble in the aqueous solutions of other aluminium salts. One equivalent of aluminium sulphate, $\text{Al}_2 (\text{SO}_4)_3$, can keep one equivalent of aluminium phosphate, AlPO_4 , in solution, according to Liechti and Suida.* This is probably the reason why sodium phosphate is not a good fixing agent for aluminium mordants.

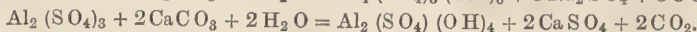
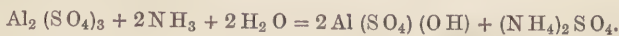
Sodium arsenate precipitates from the solutions of aluminium salts *aluminium arsenate* as a white powder, which is insoluble in water, but soluble in acids. This reaction is used to fix aluminium mordants on the vegetable fibres.

Sodium silicate precipitates from the solutions of aluminium salts aluminium hydroxide; the silicic acid does not combine under these conditions with alumina; if the silicate of soda contains an excess of caustic soda, the precipitate of aluminium hydroxide may redissolve in the precipitant.

Basic Aluminium Salts.—Aluminium salts dissolve freshly-precipitated aluminium hydroxide, forming basic salts, as exemplified in the following equation:—



Basic salts are also obtained in a soluble form by adding the requisite amount of the hydroxides or carbonates of potassium, sodium, ammonium, or calcium to the solutions of the normal salts, as shown by the following equations:—



The solutions of the basic salts are more or less rapidly dissociated into normal salts and hydroxide, which latter is precipitated. For instance:—



The dissociation is effected by heating or by dilution with water, and

* *Journ. Soc. Chem. Ind.*, 1883, p. 537.

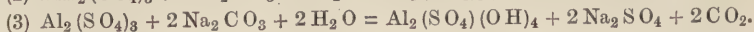
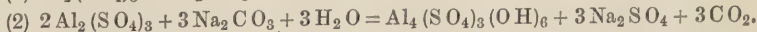
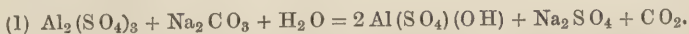
takes place the more readily the greater the basicity of the salt is. The presence of other sulphates—*e.g.*, sodium sulphate—in solution causes the basic salts to dissociate more readily.

Probably still more basic sulphates than the compound, $\text{Al}_2\text{SO}_4(\text{OH})_4$, exist. These, however, are insoluble in water.

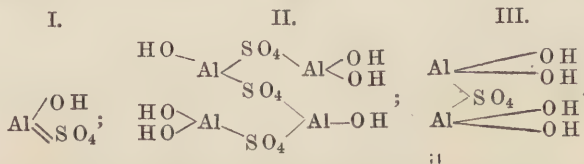
Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$.—Aluminium sulphate is prepared by dissolving aluminium oxide or hydroxide in sulphuric acid. On the large scale aluminium hydroxide (obtained from cryolite, AlNa_3F_6), or clay (aluminium silicate), or bauxite (alumina containing ferric oxide) is dissolved in sulphuric acid, and the mass is evaporated until it solidifies on cooling.

Aluminium sulphate in the pure state forms monoclinic tablets which contain 18 molecules water of crystallisation and dissolve very easily in water. In alcohol it is insoluble. The commercial article, known under the names of *cake-alum*, *patent alum*, *concentrated alum*, occurs as a solid mass or irregular lumps, having a fused appearance. It often contains more than 55 per cent. $\text{Al}_2(\text{SO}_4)_3$, and should not contain less than 48 per cent.; the pure salt, $\text{Al}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$, contains 51.35 per cent. $\text{Al}_2(\text{SO}_4)_3$. The article must be free from iron and from an excess of acid; the former injures the ultimate shade, while the latter is liable to weaken the vegetable fibres and to affect the reactions. It is not easy for the manufacturer to satisfy these demands; excellent qualities, however, are produced now which perfectly replace the more expensive alum; still aluminium sulphate should be carefully examined before use for free acid, iron, and percentage of $\text{Al}_2(\text{SO}_4)_3$, as its composition is very irregular and varies even in different parts of the same piece.

Basic aluminium sulphates are obtained, as indicated above, by adding alkalis or carbonates, &c., usually sodium carbonate, to the solutions of aluminium sulphate (or alum). The greater the amount of alkali added the greater is the basicity of the product, as shown by the following equations:—



The constitution of the basic salts is explained by the following formulæ:—



With increasing basicity the salt becomes more similar to aluminium hydroxide; thus formulæ I. shows a salt which is two-thirds a

sulphate and one-third a hydroxide; while the salt in formula III. is only one-third a sulphate and two-thirds a hydroxide. By the increase of basicity the intramolecular cohesion is greatly diminished: the normal aluminium sulphate cannot be decomposed either by boiling or by diluting with water, the basic salt I. dissociates slowly and incompletely, salt II. more readily, and salt III. very fast on boiling or diluting with water, separating gelatinous aluminium hydroxide $\text{Al}(\text{OH})_3$.

Liechti and Suida* have investigated the nature of these salts; they experimented with solutions of the normal and basic salts, which were equivalent to a strength of 200 grms. normal aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 + 18 \text{H}_2\text{O}$, per litre; they determined the effect which was produced both by boiling and by diluting with water, and they ascertained, besides, the quantities of alumina which were retained by the cotton fibre on steeping, drying, and ageing. A solution of normal aluminium sulphate—200 grms. per litre—could be boiled or diluted with water without any change, and yielded to the cotton fibre only 12.9 per cent. of its alumina; an equivalent solution of the first basic salt, $\text{Al}(\text{SO}_4)(\text{OH})$, was precipitated after being boiled for some time, or on being diluted fourteen-fold with water and gave up to the cotton fibre 51 per cent. of the available alumina; the more basic salt, $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$, began to dissociate when heated to 68° or when diluted with only twice its volume of water, and yielded as much as 58.7 per cent. of its alumina to the cotton fibre; finally, the most basic salt, $\text{Al}_2(\text{SO}_4)(\text{OH})_4$, dissociated too rapidly on diluting to be available as a mordant. It was also found, as mentioned above, that the basic salts dissociated more rapidly when other sulphates—*e.g.*, sodium sulphate—were present in the solutions. Possibly still more basic sulphates exist than those described here, which, however, are not soluble in water, and have not been prepared by precipitating aluminium sulphate with basic agents. D. Koechlin† has boiled a solution of aluminium acetate which contained basic aluminium sulphate, and thus produced a precipitate which contained for 100 parts sulphuric acid 343.5 parts alumina—*i.e.*, only $\frac{1}{10}$ of the sulphuric acid of the normal salt; whereas the soluble basic salt, $\text{Al}_2(\text{SO}_4)(\text{OH})_4$, contains one-third the sulphuric acid that the normal salt does. Basic salts, like that produced by Koechlin, are probably formed by steeping cotton in commercial red liquor (which contains aluminium sulphate-acetates, as noticed below), and subsequent drying and ageing.

Liechti and Suida have tried to obtain pure basic sulphates by dissolving freshly-prepared aluminium hydroxide in a solution of the normal aluminium sulphate; they did not succeed, however, in obtaining very basic sulphates. On gradually adding aluminium hydroxide to the normal sulphate, sufficient to form the basic com-

* *Journ. Soc. Chem. Ind.*, 1833, p. 537.

† *Schuetzenberger, Farbstoffe*, II., p. 210.

pound, $\text{Al}_2(\text{SO}_4)_3(\text{OH})_6$, no alumina at all dissolved, and, on filtering, the solution was found to contain normal sulphate only, but no basic salt. It is supposed that the nascent basic compound became decomposed as follows:—



Alum—*Potash Alum*, $\text{Al}_2\text{K}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$; *Ammonia Alum*, $\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$.—The name “Alum” originally indicated the double sulphate of aluminium and potassium which crystallises in the shape of octahedra, with 24 molecules of water of crystallisation. The name was extended later to a whole class of double sulphates of analogous constitution and isomorphous form. In these, either aluminium is substituted by another metal, which forms a sesquioxide analogous to alumina (Al_2O_3)—*i.e.*, by chromium, iron, or manganese; or potassium may be replaced by another monovalent metal; or both aluminium and potassium may be exchanged in this way. Thus a great number of “alums” are known; for instance:—

Ammonia alum,	. . .	$\text{Al}_2(\text{NH}_4)_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$.
Soda alum,	. . .	$\text{Al}_2\text{Na}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$.
Chrome alum,	. . .	$\text{Cr}_2\text{K}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$.
Ferric-ammonia alum,	. . .	$\text{Fe}_2(\text{NH}_4)_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$.

All these alums crystallise in octahedra, and cannot be separated by crystallisation when present in solution together.

Commercial alums—*i.e.*, both potash alum and ammonia alum—are obtained by various processes, the ultimate aim of which is to produce a mixed solution of aluminium sulphate and potassium or ammonium sulphate. This mixture is allowed to crystallise, and is purified by recrystallisation.

Alum, as indicated, crystallises in large octahedra with 24 molecules of water of crystallisation. The solubility of potash and ammonia alum in water is given in the following table. Soda alum is much more soluble in water, but cannot easily be obtained in crystals; it is, consequently, not a commercial article. The alums are not soluble in absolute alcohol. 100 parts of water dissolve at—

	10° C.	20° C.	30° C.	40° C.	70° C.	100° C.
Parts potash alum, .	9.5	15.1	22.0	30.9	90.7	357.5
Parts ammonia alum, .	9.1	13.6	19.3	27.3	72.0	421.9

Alum is not dissociated by boiling or by diluting with water. By the addition of caustic alkalies or alkaline carbonates to solutions of alum, so-called “neutral” and “basic” alums are obtained which are both analogous to the basic aluminium sulphates, and likewise decompose on boiling and on diluting. By gradually adding the alkali

temporary precipitates are formed which redissolve on stirring, but become permanent on adding more alkali. A solution of alum which has been rendered as alkaline as possible without permanent precipitation, has a neutral reaction, and is called by dyers "neutral alum;" it is, however, a basic salt. It can be prepared by boiling a solution of 12 parts of alum with 1 part calcium hydroxide. If it is allowed to evaporate slowly at the ordinary temperature, crystalline crusts are formed, which contain the basic salt, $\text{Al}_4(\text{SO}_4)_3(\text{OH})_6$, and potassium sulphate (if potash alum was used). If the solution is heated above 40°C ., ordinary alum and a precipitate of the composition $\text{Al}_2(\text{SO}_4)(\text{OH})_4 + \text{K}_2\text{SO}_4$ is obtained.

Alum is used by dyers in preference to cake-alum, since the crystalline form assures regular composition. It is, however, being gradually replaced by the latter, which is now sold at low prices in excellent qualities. Potash alum contains only 36.1 per cent. $\text{Al}_2(\text{SO}_4)_3 = 10.76$ per cent. Al_2O_3 ; and ammonia alum 37.7 per cent. $\text{Al}_2(\text{SO}_4)_3 = 11.27$ per cent. Al_2O_3 ; whereas, good brands of aluminium sulphate contain over 55 per cent. pure $\text{Al}_2(\text{SO}_4)_3 =$ over 16.4 per cent. Al_2O_3 . No distinction is made in practice between potash and ammonia alum, but the latter is generally employed since it is cheaper; on the whole, both behave like aluminium sulphate. The basic salts, however, which are obtained from the alums, are disposed to dissociate more rapidly than those from aluminium sulphate, on account of the quantity of potassium or ammonium sulphate they contain.

Aluminium Chloride, AlCl_3 or Al_2Cl_6 .—Aluminium chloride in the anhydrous state is obtained by passing a current of chlorine over a heated mixture of aluminium oxide and charcoal. For practical purposes, aluminium chloride is manufactured by double decomposition of the sulphate with barium or calcium chloride; or by dissolving aluminium hydroxide in hydrochloric acid; this product contains water, which cannot be entirely removed without decomposition of the salt.

The anhydrous compound forms a white crystalline mass which can be volatilised; it is readily soluble in water, alcohol, and ether, and is deliquescent in the air; in a moist atmosphere it gives off fumes of hydrochloric acid. From the aqueous solutions, crystals having the composition $\text{AlCl}_3 + 6\text{H}_2\text{O}$ are obtained, which decompose readily by heat into hydrochloric acid, aluminium oxide or hydroxide, and water. The solution is not decomposed either on boiling or on diluting with water. The article is sold in the form of a strong solution.

Basic aluminium chlorides or oxychlorides are obtained by adding the requisite amount of sodium carbonate to the solution of the normal chloride. Liechti and Suida (*l.c.*) prepared the following basic chlorides in solution:—

1. $\text{Al}_2\text{Cl}_5(\text{O H}) = \text{Al Cl}_3 + \text{Al Cl}_2(\text{O H})$.
2. $\text{Al}_2\text{Cl}_4(\text{O H})_2 = 2 \text{Al Cl}_2(\text{O H})$.
3. $\text{Al}_2\text{Cl}_3(\text{O H})_3 = \text{Al Cl}_2(\text{O H}) + \text{Al Cl}(\text{O H})_2$.
4. $\text{Al}_2\text{Cl}_2(\text{O H})_4 = 2 \text{Al Cl}(\text{O H})_2$.

None of these solutions is dissociated either by heating or diluting with water. By dissolving aluminium hydroxide in aluminium chloride only the first two basic salts could be obtained. To a solution of aluminium chloride a quantity of aluminium hydroxide was added, sufficient to form the basic salt, $\text{Al Cl}_2\text{O H}$. The alumina dissolved only on heating, and the solution remained clear on cooling. To this clear solution a further quantity of aluminium hydroxide was added, sufficient to form the compound, $\text{Al Cl}(\text{O H})_2$. No more alumina, however, could be made to dissolve, the precipitate even increased, and on filtering it was found that the solution contained 1 equivalent of hydrochloric acid, H Cl , for 2 equivalents of aluminium chloride, Al Cl_3 . The nascent $\text{Al Cl}(\text{O H})_2$ had apparently decomposed according to the equation—

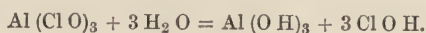


A similar behaviour was shown by aluminium sulphate (see above).

The aluminium chlorides yield but small quantities of alumina to the fibre, and are rarely used as mordants. A process of carbonising vegetable matter in wool is based on the property which aluminium chloride has of decomposing when its aqueous solution is evaporated to dryness. Woollen rags are simply saturated with a solution of normal aluminium chloride and dried after the excess of liquid has been removed by mechanical means; the hydrochloric acid which is liberated destroys the vegetable fibre without affecting the colours.

Aluminium chloride has antiseptic properties, and was offered some time ago as a disinfecting agent.

Aluminium Hypochlorite, $\text{Al}(\text{Cl O})_3$ (?) — *Wilson's Bleaching Liquor*.—Aluminium hypochlorite is obtained in solution by the double decomposition of aluminium sulphate and chloride of lime solutions. The compound is very prone to decompose into aluminium chloride and oxygen, and can be used as a bleaching agent without any acid being added. Four parts of aluminium hypochlorite (calculated on $\text{Al}(\text{Cl O})_3$) are diluted with 200 parts of water, and the goods steeped in this solution for 2 to 3 hours. The compound has also been recommended as a mordant, since it decomposes on the fibre into aluminium hydroxide and hypochlorous acid—



On the whole, this substance offers no special advantage for the bleaching and dyeing of the textile fibres, and the fact that it readily decomposes is counterbalanced by the generation of aluminium chloride, which rapidly destroys the vegetable fibre. The antiseptic

properties of aluminium chloride, however, render it available for other manufactures—*e.g.*, paper making.

Aluminium Nitrate, $\text{Al}(\text{NO}_3)_3$.—This salt is obtained by dissolving aluminium hydroxide in nitric acid, or by double decomposition of the sulphate with nitrate of lead or barium. The salt forms crystals with 9 molecules of water, which are very soluble and deliquescent, and when heated to 150° are decomposed into nitric acid, aluminium oxide, and water.

Basic aluminium nitrates can be obtained by adding the requisite quantities of sodium carbonate to the solution of the normal salt; neither the normal nor the basic aluminium nitrates are dissociated by heating or by diluting with water.

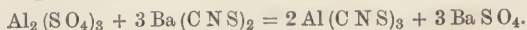
Aluminium nitrate has a limited application in the production of steam colours on calico; it is not used as a mordant for wool or silk.

Aluminium Sulphite, $\text{Al}_2(\text{SO}_3)_3$ (?); **Aluminium Bisulphite**, $\text{Al}(\text{SO}_3\text{H})_3$ (?).—Aluminium sulphite or bisulphite has been introduced recently into commerce. It is obtained by dissolving aluminium hydrate in a strong solution of sulphur dioxide in water (sulphurous acid). The solutions are readily decomposed on boiling.

Aluminium Thiosulphate (*Hyposulphite*).—This salt is obtained by double decomposition of aluminium sulphate and calcium thiosulphate. It is known in solution only, and its exact composition has not been determined.

Aluminium thiosulphate was prepared by E. Kopp as early as 1856. He found that the aqueous solution readily decomposes on boiling, into aluminium hydroxide, sulphur dioxide, and sulphur; and recommended it to calico printers as a mordant, its advantages being that it was cheaper than aluminium acetate, that it fixed the alumina better on the fibre than the other salts; and that it prevented, by its reducing action, the oxidation and fixation of iron on the fibre. This mordant, however, has not found general application, since it gives off sulphur dioxide even on drying on the cylinders, and deposits sulphur together with the alumina on the fibres; hence its employment is not advisable. Recently a solution containing alum and sodium thiosulphate has been proposed for mordanting silk previous to dyeing with the alizarins. It is said to have yielded good results on the large scale.

Aluminium Thiocyanate or **Sulphocyanide**, $\text{Al}(\text{CNS})_3$.—Aluminium thiocyanate is obtained by the double decomposition of aluminium sulphate with barium or calcium thiocyanate:—



Care must be taken that the aluminium sulphate does not contain any excess of acid; if it does, it must be neutralised by an alkaline thiocyanate, preferably sodium or ammonium thiocyanate. Sulphuric acid in the free state would be liable to cause a tendering of the fibre on drying and steaming, and to carry iron into the colour, whereas the neutral thiocyanates do not affect the fibres nor exert a corroding

action on iron. Aluminium thiocyanate of 32° Tw. strength is made by dissolving the following ingredients at 60° C. :—

3 kgs. (30 lbs.) cake-alum in
2.5 litres (2½ galls.) water ;
and
4.1 kgs. (41 lbs.) barium thiocyanate in
2.5 litres (2½ galls.) water.

Mix the two solutions, filter from the white precipitate, wash with water, dilute with the washing liquor till the strength is 32° Tw.

The crude calcium thiocyanate solutions can also be used—

5 kgs. (10 lbs.) cake-alum are dissolved in
5 litres (1 gall.) boiling water, then
250 grms. (½ lb.) chalk, and
11½ litres (2⅔ galls.) calcium sulphocyanide 32° Tw. are added.

If necessary the mordant can be concentrated by boiling over a fire.

Liechti and Suida examined the normal and basic aluminium thiocyanates. The normal salt can be boiled, and even concentrated by boiling, to a syrupy consistency without being decomposed. The salt, $\text{Al}_2(\text{CNS})_5\text{OH}$, is also stable; but the more basic salts are decomposed when boiled; mere dilution with water will not cause the decomposition of any of these salts.

Aluminium thiocyanate was introduced some years ago by Storck for the production of alizarin-reds in calico-printing as a substitute for aluminium acetate. It possesses the great advantage that it does not attack the steel doctors of the printing machine, and thus does not introduce iron into the printing colour; hence the purity and brilliancy of alizarin-red is preserved. The high price of the article has prevented its more general employment, especially in wool dyeing. Very fine results are obtained by mordanting this fibre with aluminium thiocyanate. The wool is introduced into the cold mordanting bath, which is gradually heated to boiling during 1 to 1½ hours. Silk may be mordanted like wool. The thiocyanate is also used in silk-printing.

Aluminium Acetate, $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ or $\text{Al}_2(\text{C}_2\text{H}_3\text{O}_2)_6$.—Normal aluminium acetate is not known in the pure state. The solution is obtained by dissolving aluminium hydroxide in acetic acid, or by the double decomposition of aluminium sulphate and lead- or calcium acetate—

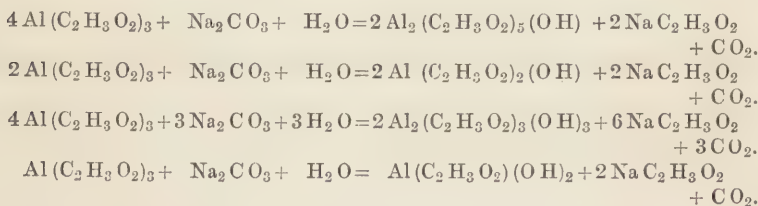


The solution of normal aluminium acetate smells of acetic acid, and yields the basic acetate, $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})$, in the solid state, but containing various amounts of water, according to the different conditions under which it is formed.

$\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH}) + 4\text{H}_2\text{O}$ is obtained by rapid evaporation of the solution of the normal acetate below 38° C. as a soluble gummy substance, which does not smell of acetic acid. $2(\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_2\text{OH})$

+ 5 H₂ O is formed as a hard porcelain-like insoluble mass when the solution of the normal acetate is allowed to stand some days at ordinary temperatures. 2 (Al (C₂ H₃ O₂)₂ O H) + 3 H₂ O is precipitated as an insoluble crystalline glittering substance on heating the concentrated solution of the normal acetate; the precipitate which forms on the bottom of the vessel is formed the more rapidly the higher the temperature (at 37° C. in some days; at 60° C. in some hours; at the boiling point at once); the supernatant liquor contains scarcely any aluminium. This last-named basic salt is insoluble in cold or warm water and in acetic acid; it dissolves in mineral acids, in aluminium sulphate, and in large quantities of boiling water. Freshly-prepared solutions of the normal acetate, containing less than 3 per cent. of this salt, are not decomposed by boiling; after some weeks they dissociate, forming basic salts and free acid, and become more liable to decomposition when boiled. Solutions of the normal acetate which contain other salts (like the alkaline sulphates or chlorides or alum) become turbid when heated, and form precipitates when boiled much more readily than the pure acetate; they dissociate, forming acetic acid in the free state, and precipitates of basic acetates, which redissolve on cooling, unless the acetic acid has been driven off by prolonged boiling. These results, which were obtained many years ago by Walter Crum,* are not in harmony with the more recent researches of Liechti and Suida (*l.c.*). The latter state that normal aluminium salts are not dissociated either by heating or by diluting with water.

By adding to the solution of normal aluminium acetate the requisite amounts of sodium-carbonate solutions of basic acetates of varying basicity are obtained, as shown by the following equations:—



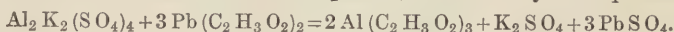
The solutions of basic acetates are dissociated on heating; the more basic they are the lower is the temperature at which the dissociation begins; but the dissociation is retarded by dilution with water; in the absence of alkaline sulphates no dissociation is effected by diluting with water at the ordinary temperature. The precipitates formed by basic acetates in the absence of sulphates at higher temperatures are not redissolved on cooling. They seem to consist chiefly of aluminium hydroxides.

Comparative experiments were made by Liechti and Suida as to the

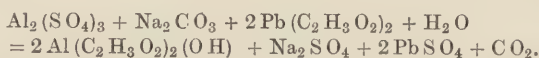
* *Liebig's Ann.*, 89, p. 156.

mordanting power of normal and basic acetates. They used solutions of $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_3$ and $\text{Al}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})$, equivalent to 200 grms. normal sulphate per litre, and impregnated pieces of calico with such solutions until the cloth had taken up an amount of the respective solutions equal to its own weight; the cloth was then dried, aged, and washed in equal quantities of water to remove all the aluminium which had not been fixed; under these circumstances only one-half of the alumina in the normal salt, while all that in the basic salt was taken up in the fixing.

In the presence of alkaline sulphates—*e.g.*, sodium sulphate—both the normal and the basic aluminium acetates are dissociated by diluting with water, and the dissociation by heat proceeds more readily than in the absence of sulphates. The precipitates obtained by heating redissolve on cooling if formed in the presence of soluble sulphates. The acetates which are obtained from alum and lead- or calcium acetate, always contain soluble sulphates, as shown by the equation—



In practice the basic acetates are prepared by the double decomposition of aluminium sulphate partly with acetate of lead or calcium, partly with sodium carbonate, as is indicated by the following equation:—

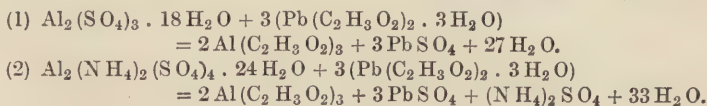


Both in this case, and when the acetate is prepared from alum, the product contains a soluble sulphate, and is thereby more easily dissociated.

It appears that the precipitates which are formed in the presence of sulphates always contain some sulphuric acid, and consist of a very basic sulphate. (See p. 222—the analysis of D. Koechlin).

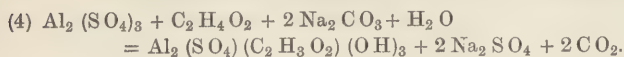
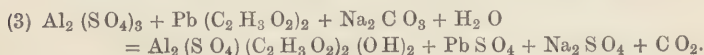
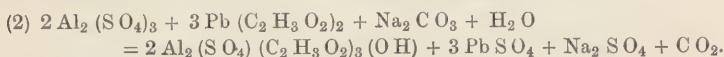
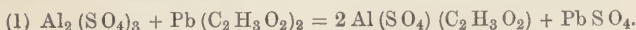
Aluminium acetates, which are prepared with lead acetate, are liable to retain in solution some lead in the form of lead sulphate, which may exert an injurious influence; therefore, in certain cases (for instance, in steam alizarin-reds), the lead acetate is replaced by calcium acetate. Lead sulphate, however, although perceptibly soluble in aluminium acetate, is found only in traces in solutions which contain soluble sulphates—such as those of sodium or aluminium.

Aluminium Sulphate-Acetates or Sulpho-Acetates.—171 parts of crystallised lead acetate are required to convert 100 parts of aluminium sulphate into normal aluminium acetate; and for 100 parts of potash alum or ammonia alum 120 and 125 parts respectively of the lead salt are required, in conformance with the two equations—



In practice a very much smaller amount of lead acetate is usually employed, and this is still further reduced, if a part of the sulphuric acid is neutralised by the addition of soda or chalk, to produce a basic salt. Thus mixtures of normal or basic sulphates and of normal acetate of aluminium are obtained, which are known as *sulphate-acetates* or *sulpho-acetates*. The investigations of Koechlin-Schouch and of D. Koechlin have proved—in harmony with long practical experience—that these aluminium sulphate-acetates deposit in the cotton fibre, by impregnating, and subsequent ageing, basic sulphates which possess the same mordanting properties as the hydroxides of aluminium. A precipitate of pure basic aluminium sulphate was prepared from alum, dissolved in acetic acid, and fixed on the fibre by impregnating and ageing. The compound which was deposited in the fibre in this way must be a basic aluminium sulphate, according to the method of its preparation. Its value for dyeing was ascertained by a practical dye test with madder, and it proved, indeed, an excellent mordant.

The recent investigations of Liechti and Suida (*l.c.*) confirm this opinion. These authors prepared sulphate-acetates in accordance with the following equations* :—



The normal sulphate-acetate, $\text{Al} (\text{SO}_4) (\text{C}_2 \text{H}_3 \text{O}_2)$, does not dissociate when diluted with water, although, when heated, the basic sulphate-acetates are decomposed by both agencies, while increase in basicity lowers the dissociation point both on heating and on diluting. The precipitates are formed as jelly-like substances at temperatures from 89° to 40° C. The precipitate of the normal sulphate-acetate redissolves on cooling the solution, that of $\text{Al}_2 (\text{SO}_4) (\text{C}_2 \text{H}_3 \text{O}_2)_3 \text{OH}$ partially; whereas the precipitates formed by heating the more basic sulphate-acetates are permanent. All these sulphate-acetates—normal and basic—yield nearly the whole of their alumina to the fibre during mordanting, drying, and ageing; and, therefore, in this respect, they are much stronger mordants than the sulphates.

Red Liquor.—The commercial solutions of acetates and sulphate-acetates of aluminium are known in the trade as *red liquor*, because they are employed by cotton dyers and calico printers as mordants for alizarin-reds. The composition of the red liquors varies greatly, and

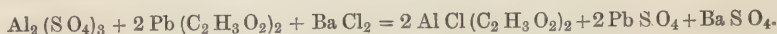
* In these equations the water of crystallisation—18 equivalents for aluminium sulphate and 3 equivalents for lead acetate—have been omitted; they must be taken into account in calculating the proportions for practical purposes.

their value for different styles of work is better determined by practical tests than by analysis. They are prepared by the double decomposition of normal aluminium sulphate and commercial acetate or pyrolignite of lime, with or without addition of chalk or soda, and have always a yellowish-brown appearance, from the presence of empyreumatic substances; their strength varies from 1.08 to 1.12 sp. gr.

Lauber * gives the following proportions for the preparation of red liquor:

1.	2.
189 kgs. (189 lbs.) alum,	40 kgs. (40 lbs.) cake-alum,
161 kgs. (161 lbs.) yellow sugar of lead, and	50 kgs. (50 lbs.) yellow sugar of lead,
450 litres (45 galls.) water.	1½ kgs. (1½ lbs.) chalk, and
	90 litres (9 galls.) water.

Aluminium Chloride-Acetate, $\text{Al Cl (C}_2\text{H}_3\text{O}_2)_2$. — Liechti and Suida prepared a salt of this composition according to the following equation:—



They found that this salt does not dissociate either on heating or on diluting, and yields to the cotton fibre by steeping, drying, and ageing the remarkably low amount of 3.26 per cent. alumina.

Aluminium Nitrate-Acetate, $\text{Al (N O}_3)(\text{C}_2\text{H}_3\text{O}_2)_2$, is obtained by double decomposition of aluminium sulphate with the acetate and nitrate of calcium or lead, and is used as a mordant for calico-printing and silk dyeing. It is valuable for the production of fine steam alizarin-reds, since it is very gradually dissociated on steaming.

Aluminium Oxalate, $\text{Al}_2(\text{C}_2\text{O}_4)_3$ (?). — Aluminium oxalate in the pure state has not been prepared.

Aluminium hydroxide dissolves in oxalic acid; the solution yields, on evaporating, an amorphous, deliquescent mass. The solutions of aluminium salts are not precipitated by oxalic acid or its salts. Aluminium oxalate, obtained by dissolving the hydroxide in oxalic acid, is limited in its use to certain steam colours for calico-printing. If oxalic acid is used in mordanting wool with aluminium sulphate, the oxalate is formed to some extent, and takes part in the mordanting process. The oxalate itself, however, is not used in wool or silk dyeing. Regarding the behaviour of aluminium oxalate as a wool-mordant see p. 237.

Aluminium Tartrate.—This salt has not been prepared yet in the pure state, although it is a very important substance in wool dyeing, being formed by the double decomposition of aluminium sulphate and acid potassium tartrate (tartar) in the mordanting bath (see p. 238).

Aluminium hydroxide, dissolved in tartaric acid, is also used in a few steam colours in calico-printing.

* *Handbuch des Zeugdrucks.*

APPLICATION OF THE ALUMINIUM SALTS TO THE TEXTILE FIBRES.

Aluminium sulphate and alum are often used as mild acidifying agents, instead of sulphuric acid, in the dye-bath—*e.g.*, in the dyeing of soluble blue on cotton and of acid colours on wool. If so employed they cannot be considered as mordants in most cases, none of their constituents becoming parts of the ultimate colour.

Application to Cotton and Linen—(1) *Aluminium Sulphate and Alum*.—Normal aluminium sulphate or alum yield but very little alumina to the fibre (13 per cent. according to Liechti and Suida, see p. 222). They are used for the mordanting of cotton in exceptional cases only, as, for instance, when a dyestuff of great tinctorial power is used. The cotton is impregnated with a solution of alum, wrung out, passed without washing, through a solution of sodium carbonate at 50° to 60° C. for 20 minutes and thoroughly washed in water. Use for 10 kgs. (10 lbs.) cotton, 1 kg. (1 lb.) alum, and $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) soda crystals in 200 litres (20 galls.) water. Methyl violet yields on this mordant brighter though less fast shades than on tannin and antimony.

The basic salts are usually employed for the mordanting of cotton with aluminium sulphate. The basic sulphate corresponding to the formula $\text{Al}(\text{S O}_4)(\text{O H})$ is prepared by dissolving 2 kgs. (6 lbs.) pure aluminium sulphate, $\text{Al}_2(\text{S O}_4)_3 + 18 \text{H}_2\text{O}$, in 10 litres (3 galls.) water, and adding gradually a cold solution of 330 grms. (1 lb.) soda ash (58°) in $2\frac{1}{2}$ litres (3 quarts) water. During the mixing the mass is vigorously agitated by stirring, and fresh portions of soda are added only after the precipitate first formed has redissolved. The solution is diluted to about 10° to 12° Tw. To obtain the compound free from other salts the aluminium sulphate can be completely precipitated as the hydroxide, washed, and redissolved in diluted sulphuric acid; for 2 kgs. (10 lbs.) aluminium sulphate, 1 kg. (5 lbs.) soda ash (58°), and 600 grms. (3 lbs.) sulphuric acid (168° Tw.) are necessary. In case the alum-cake should contain more or less than 51.35 per cent. $\text{Al}_2(\text{S O}_4)_3$ —as demanded by the formula $\text{Al}_2(\text{S O}_4)_3 + 18 \text{H}_2\text{O}$ —more or less is used to obtain exactly the same product; if it contains an excess of sulphuric acid a correspondingly larger amount of soda ash is employed.

The salt produced in this way, $\text{Al}(\text{S O}_4)(\text{O H})$, is probably the most generally employed of the basic sulphates. We have seen that it yields over 50 per cent of its alumina to the cotton fibre on steeping, drying, and ageing. Liechti and Suida consider the salt, $\text{Al}_4(\text{S O}_4)_3(\text{O H})_6$, the best mordant, as it gives up under the same conditions nearly 60 per cent. of its alumina; but this salt appears to be too prone to decompose on diluting with water to be a good mordant.

Two essentially different methods are employed in mordanting cotton with basic aluminium sulphate:—

(1) The material is impregnated directly with the mordant and the latter fixed by other chemicals or by ageing ;

(2) The material is first impregnated with a substance which attracts the basic sulphate and forms an insoluble compound with alumina (oil mordants, tannic acid), or which deposits alumina in an insoluble form in the fibre by double decomposition (stannate of soda) ; after this treatment follows the mordanting with basic aluminium sulphate or alum ; a further fixing of the alumina mordant is sometimes necessary.

Direct Mordanting with Basic Aluminium Sulphate.—The cotton is turned for some time in the above described solution of the basic sulphate and left in the bath for 3 to 5 hours, wrung and dried. More alumina is fixed if the impregnating of the material with the mordant is followed by ageing. The vegetable fibre, however, is liable to be weakened by the free acid or acid salts of aluminium which are formed thereby. Loose cotton or cotton yarn would, besides, give uneven shades through unequal drying, and, consequently, unequal decomposition of the basic salt. For these reasons it is preferable to impregnate the goods with basic sulphate and to pass them subsequently through the solution of a salt which is capable of fixing the alumina on the fibre, either by precipitating it in the free state or by combining with it in the form of an insoluble salt (*e.g.*, arsenate of soda). A great number of fixing agents have been referred to on previous pages and are actually used under different conditions. The material which has been impregnated with the basic aluminium sulphate is wrung out, dried at a low temperature, and worked for half an hour in the luke-warm fixing bath. After a thorough washing it is ready for dyeing. The fixing liquor is prepared so that each litre (10 galls.) shall contain 5 to 10 grms. ($\frac{1}{2}$ to 1 lb.) of either of the following salts :—Arsenate, phosphate, or silicate (100° Tw.) of soda, sodium carbonate, ammonium carbonate or chalk ; of ammonia liquor about 50 grms. (5 lbs.) per litre (10 galls.) are used ; a soap solution containing 1 per cent. neutral soap is also sometimes employed ; the application of cow-dung has been previously explained under *Ammonium Carbonate*.

Mordanting with Basic Aluminium Sulphate after previous impregnation of the Cotton with other Substances.—The process of mordanting cotton with olive oil or sulphated oil, also with tannic acid, and subsequently with basic sulphate of aluminium is employed notably in Turkey-red dyeing, and will be fully described under that heading.

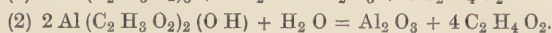
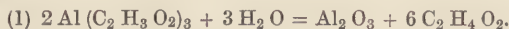
For other colours the cotton is impregnated with a solution of about 100 grms. (1 lb.) neutralised Turkey-red oil per litre (1 gall.), wrung or squeezed, dried in a stove, and worked for half an hour in the previously described solution of basic aluminium sulphate (10° to 12° Tw.) ; after this the cotton is washed in water and passed through a weak soap-bath (1 part of soap in 1,000 parts of water) to fix the

alumina thoroughly and to remove all excess of mordant. A final thorough rinsing in water makes the material ready for dyeing. In place of Turkey-red oil an equal amount of neutral soap may be employed. Tannic acid is used in a similar way.

For certain colours, especially the eosins, cotton is steeped in a tepid solution of stannate of soda for 2 to 3 hours, wrung evenly, steeped for 2 to 3 hours in partially neutralised alum, wrung again, and dyed without washing. For 10 kgs. (10 lbs.) of cotton, $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) stannate of soda, $\frac{1}{2}$ kg. ($\frac{1}{2}$ lb.) alum, and 100 grs. ($1\frac{1}{2}$ oz.) soda crystals are used.

The composition of the mordant which is retained by the fibre varies with the different fixing processes. In almost every case aluminium hydroxide is formed either by mere dissociation of the aluminium salt, or by decomposition of the same with ammonia, or with sodium or ammonium carbonate, or with chalk, &c. In addition, arsenate and phosphate of soda generate more or less aluminium arsenate and phosphate; soap produces stearate, palmitate, or oleate of aluminium; whereas silicate of soda forms the hydroxide only. If the material was prepared with tannic acid, oil or soap, tannate, &c., of aluminium is formed; the mordanting with stannate and alum produces only stannic hydrate and aluminium hydroxide. In case a basic sulphate is fixed exclusively by ageing, very basic sulphates are formed, which being insoluble in water are retained, together with the hydroxide, while the neutral sulphate and free acid, which were formed by dissociation through ageing, are removed by washing. It is, however, more usual to pass the goods after the ageing through some fixing bath—*e.g.*, chalk or phosphate, which remove probably the whole amount of the sulphuric acid.

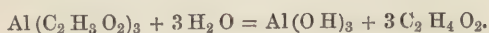
(2) *Aluminium Acetate and Sulphate-Acetate; Red Liquor.*—These mordants are not extensively used by the ordinary cotton dyer, since they are more costly than the basic sulphates, and possess no advantage over these in the general methods of fixing by precipitation. They can, however, be employed exactly like the basic sulphates, and are frequently used by Turkey-red dyers to replace the sulphates entirely or in part. Goods which have been impregnated with the acetates and sulphate-acetates must not be dried at high temperatures, since these compounds are most readily dissociated on the fibre by heat, when acetic acid escapes and the base remains on the fibre in a form which renders it less capable of combining with the colouring matter in the subsequent dye-bath; poor and irregular colours would thus result. This fact may be due to the generation of aluminium oxide instead of the hydroxide, as shown by either of the following equations:—



Another explanation is that a basic acetate or a less hydrated alumi-

niun hydroxide is formed, neither of which forms colour lakes. Mordants that have been spoiled by overheating are said to have been "burned."

In the ordinary course of treatment the mordanted goods are not always passed directly into the fixing bath, but are first subjected to the so-called *ageing process*, which has already been mentioned several times. The ageing consists in exposing the mordant in the fibre to the action of warm and moist air. In the case of aluminium acetate, the object of the ageing process is to decompose the salt, and to deposit the base in the hydrated form in the fibre, the acid being partially or wholly volatilised :



Aluminium acetates in which a part of the acetic acid has been replaced by other acids, especially sulphuric acid, yield richer colours by the ageing process than the pure acetate, the latter being probably decomposed too rapidly. Aluminium sulphate-acetate, $\text{Al}_2(\text{SO}_4)(\text{C}_2\text{H}_3\text{O}_2)_3\text{OH}$, seems to give the most satisfactory results and to yield nearly the whole of its aluminium to the fibre. In this case, as with basic aluminium sulphate, a very basic aluminium sulphate in an insoluble state is fixed together with aluminium hydroxide. A similar salt seems to be fixed, if an aluminium acetate which contains another soluble sulphate is subjected to ageing.

With the chemical fixing agents like ammonia, arsenate of soda, &c., the red liquor mordants yield the same products as the sulphates of alumina.

The acetates and sulphate-acetates of aluminium are principally employed by calico-printers. The acetates are used in steam colours when dyestuff and mordant are printed on the cloth together in the form of a mechanical mixture, and the colour is "developed" on or in the cloth by "steaming;" the normal acetate is generally used, and acetic acid in the free state is added to the colours to prevent a premature decomposition of the mordant. The sulphate-acetates are employed when the cloth is first mordanted, and then subjected to the ageing process, the dyeing process following.

Certain basic colours, especially Victoria-blue and night-blue, are dyed in conjunction with aluminium acetate on cotton which has been previously mordanted with tannin and antimony. During the gradual raising of the temperature the acetate is dissociated in the fibre, and the hydroxide in the nascent state attracts some of the colouring matter.

The other aluminium salts are not frequently used as mordants on cotton. They have been fully described before. As to aluminate of soda, see p. 219.

Application to Jute.—Jute, as a rule, is dyed without mordants. Aluminium sulphate and alum are used as acidifying agents for the

dyeing with acid dyestuffs in the same way as in wool dyeing. In many cases, either of the two salts is added to the dye-bath, together with, or without acetic, tartaric, or sulphuric acid. For some colours jute is boiled in alum solution, and passed through carbonate of soda before dyeing. This is done for certain azo-colours, like scarlet 3 R, which are too easily soluble in an acid bath to dye well.

Application to Wool.—Wool essentially differs from cotton in its behaviour towards the aluminium salts, and is mordanted in a totally different way. The investigations of Liechti and Schwitzer* have thrown much valuable light on the reactions which take place in mordanting wool.

Recent experiments have shown that wool takes up sulphuric and hydrochloric acid in the free state, retaining them with such force that they are only removed by repeated boiling out with water.

In a similar manner salts are taken up. The wool fibre possesses both basic and acid character, and seems to dissociate the salts by combining both with the acid and with the base, the base being taken up either in the free state or in the form of a basic salt. This reaction takes place most completely at the boiling point. Aluminium sulphate, for instance, is most readily decomposed by the wool fibre into basic sulphates and free acid, especially at or near the boiling temperature. The alumina which is thus taken up is retained in an insoluble form with considerable force by the fibre; no fixing agents are required, as is the case with cotton; the fixation takes place simultaneously with the impregnation in the mordanting bath under the influence of the elevated temperature. The basic salts, which are fixed on the fibre, undergo a further decomposition by washing with water; they lose acid and become more basic, while the acid is removed by the wash water.

The wool fibre attracts, also, finely-divided precipitates from liquids, and retains them with great energy. This power of attraction is comparatively weak in cold liquids, but it increases with the temperature, so that considerable amounts of such precipitates can be attached to the wool by prolonged boiling, although not fast enough to resist washing and rubbing. By the action of the wool fibre on aluminium sulphate, a precipitate of basic aluminium sulphate may be produced and boiled on to the wool fast enough to resist washing with water, although it is only mechanically fixed on the surface of the fibre. These superficially fixed mordants produce in dyeing colour lakes, which adhere still more loosely to the surface of the fibre, and possess in a high degree the defect of rubbing.

On the contrary, mordants which have entered into an intimate combination with the substance of the fibre are less liable to produce colour lakes which rub off. To attain this end the mordanting salt must possess a certain resistance to the dissociating action of the wool,

* *Journ. Soc. Dyers and Col.*, 1886, p. 161.

so as to allow of its penetrating into the interior of the fibre before it is decomposed and fixed, and of the dissociation and absorption taking place simultaneously, without the intermediate formation of a precipitate in the liquor, which might be attracted and mechanically fixed by the wool.

Taken as a whole, the salts of oxalic and tartaric acid fulfil these conditions best—a fact that reminds us of the property of the non-volatile organic acids to impede the precipitation of aluminium hydroxide by alkalies or other agents.

On the other hand, the basic aluminium sulphates are entirely unsuitable for the mordanting of wool, because they dissociate before they are taken up by this fibre.

Liechti and Schwitzer have compared *the action of sulphate, oxalate, and tartrate of aluminium in mordanting*. They prepared solutions of aluminium oxalate, $\text{Al}_2(\text{C}_2\text{O}_4)_3$, and of aluminium tartrate, $\text{Al}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, by dissolving 2 equivalents of aluminium hydroxide, $\text{Al}(\text{OH})_3$, in 3 equivalents of oxalic and tartaric acid respectively. If wool is boiled in a solution of *normal aluminium sulphate* the bath becomes exhausted if less than 5 per cent. sulphate (of the weight of the wool) is used. Larger amounts leave increasing proportions in the liquor. The mordanting baths become turbid on boiling by separating an insoluble basic aluminium salt. A part of the precipitate thus formed becomes mechanically fixed, and is removed on washing, the wash waters being turbid; a part remains in the mordanting liquor. The wool which has been mordanted gives an acid wash water on treatment with boiling water—thus proving that the aluminium sulphate has been decomposed, and that not merely alumina but free acid has been extracted from the mordanting bath. If *sulphuric acid* is added to the mordanting bath, the decomposition of the mordant is less rapid, and it is better fixed than when the normal sulphate is used alone. Comparatively large quantities of sulphuric acid are necessary—more than 3 equivalents H_2SO_4 of the sulphate, $\text{Al}_2(\text{SO}_4)_3$, and the effect of the acid decreases with an increasing dilution of the bath.

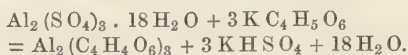
Alum is a somewhat less efficient mordant than aluminium sulphate; this is evidently due to the dissociating effect which is exerted by the alkaline sulphates present in the former salt.

Normal aluminium oxalate, $\text{Al}_2(\text{C}_2\text{O}_4)_3$, is almost completely taken up from the mordanting bath. A smaller amount of precipitate remains in the liquor, and less can be removed from the wool than in the case of mordanting with the normal sulphate. The wool, on treatment with boiling water, gives, in this case also, an acid wash water.

Normal aluminium tartrate, $\text{Al}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, if used as the wool mordant, leaves scarcely any precipitate in the bath, and does not give up any to the wash water. On treatment with hot water, the

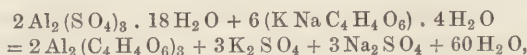
wool imparts also to the latter an acid reaction. Boiling water does not remove the mordant proper. Wool which had been boiled out several times with distilled water after mordanting, gave, on dyeing with alizarin, more brilliant and fuller colours than wool which had been simply rinsed in water.

The normal tartrate can be replaced, with excellent results, by a mixture of 1 equivalent of aluminium sulphate and 3 equivalents of tartar (acid potassium tartrate)—



In this case, as shown by the equation, a mixture of normal aluminium tartrate and acid potassium sulphate is formed.

If the normal tartrate is prepared by double decomposition—*e.g.*, with normal potassium-sodium tartrate (Rochelle salt), as in the following equation:—



the results obtained are not as good as those with the pure tartrate or with the mixture produced with tartar. These facts lead to the conclusion that the tartrate is similar to other aluminium salts, and is more rapidly dissociated in the presence of alkaline sulphates than in the pure state; and that in the case of a mixture of aluminium sulphate and tartar being used, the acid sulphate prevents a premature dissociation.

An examination of the spent mordant- and dye-baths shows that the mordanting is most perfect in the case of the tartrate, the whole of the alumina being fixed in a permanent manner.

It appears that not only the hydroxides but also true basic aluminium salts are deposited by the mordanting process in the fibre, as on dyeing the well-washed wool with alizarin, the spent dye liquors invariably show an acid reaction.

These theoretical considerations and experiments are in perfect harmony with practical experience.

Basic aluminium sulphates are not used as wool mordants, neither are the acetates or sulphate-acetates, as they dissociate too rapidly and give poor results. By depositing too much of the mordant on the surface, they make the wool harsh and give rise to uneven dyeing and rubbing. Thiocyanate of aluminium, which is not as sensitive as the acetates, is a very good wool mordant; but its general employment is prevented by its high price.

The aluminium mordant *par excellence* for wool is aluminium sulphate, either alone or in conjunction with acids or acid salts. In some cases the sulphate is used without any additions. Most generally, however, a mixture of the sulphate with tartar or tartar substitutes is required to obtain full and brilliant colours which do not rub off. These tartar

substitutes are mostly sodium bisulphate or oxalates, or they consist of tartar which has been prepared with sufficient sulphuric acid to convert all the potassium into potassium sulphate (see p. 186). From the foregoing it appears that none of these "substitutes" can replace the tartar completely, because the action of the latter depends on the formation of *aluminium tartrate by double decomposition*. They have, of course, some effect, as has also sulphuric acid. For a full shade about 6 to 8 per cent. aluminium sulphate and 5 to 7 per cent. tartar (of the weight of the wool) are necessary. The quantity of tartar may be reduced to about half this amount, or it may be partly or even wholly replaced by sulphuric, hydrochloric, oxalic acid, bisulphate of sodium, &c., with very good, although not equally fine, results. About 4 per cent. of sulphuric acid (of the weight of the wool) is used, if the amount of water does not exceed 50 to 60 times the weight of the wool; otherwise more acid must be applied. When sulphuric acid has been used in mordanting, it is often beneficial to add about 5 per cent. sodium acetate to the ultimate dye-bath to neutralise the mineral acid which always remains in the wool fibre (and which otherwise would be converted into potassium sulphate if tartar had been employed). The mordanting bath is prepared with the necessary quantities of aluminium sulphate and tartar (or its substitutes), and the wool is entered at a low temperature. During 1 to 1½ hours the bath is heated gradually to boiling, and boiled for ½ hour more. When the bath has cooled down the wool is taken out and thoroughly washed in water; boiling out with water is beneficial. It has been shown that washing is absolutely necessary to remove all loosely adhering mordants and to prevent rubbing of the ultimate colour. The washing, moreover, removes some of the acid, which is absorbed by the wool, and would be injurious in dyeing.

The washed wool is ready for dyeing; it should not be allowed to dry, as it is then very difficult to wet out again.

Application to Silk.—Silk dyers do not often use aluminium mordants; in the first place, they employ chiefly direct colours—*i.e.*, colours that do not require mordants, and in addition the alumina causes the fibre to lose some of its lustre and pliability.

The mordanting takes place at, or a little above, the ordinary temperature, to prevent the silk from losing its gloss and feel by the action of the mordant; this makes it necessary to use aluminium salts which dissociate readily. In silk dyeing, alum has not been replaced yet by aluminium sulphate, probably owing to the circumstance that slightly basic alum decomposes more readily than basic sulphate on account of the ammonium or potassium sulphate present in the former. The basic alum-bath may be prepared in the following manner:—10 parts of alum are dissolved together with 1 part of soda crystals in sufficient water for complete solution (about 150 parts), and the liquor is gently heated until the precipitate first formed has completely

disappeared. Aluminium sulphate-acetate and nitrate-acetate are used in a similar way. The silk is thoroughly wetted out, wrung evenly, and passed into the mordanting bath. It is turned a short time without heating and then allowed to soak in the liquid for 12 hours. After this it is wrung and washed in water or, preferably, passed first through a solution of silicate of soda (1° Tw.) to fix the alumina; instead of the silicate a soap-bath may be employed. The silk is finally washed in water to remove all excess of mordant and fixing agent, and is then ready for dyeing. It should not be allowed to dry after mordanting, since it is afterwards difficult to wet out again and acquires an unpleasant feel.

During the steeping process the silk absorbs basic sulphates or basic sulphate-acetates, or nitrate-acetates. By the subsequent treatment with water or silicate of soda or soap the basic salts are decomposed and aluminium hydroxide is precipitated in the fibre. On account of all solutions being used cold gelatinous hydroxide is formed, and this is less liable to exert an injurious effect on the silk than the more crystalline hydrate which is formed at higher temperatures.

The composition of the mordanting baths remains fairly constant, and they may be used continuously if they are freshened up each time.

CHROMIUM, Cr = 52.3.

Chromium is a trivalent metal, the symbol and atomic weight of which are Cr. and 52.3 respectively. It is of no practical interest as a metal. The chief ore from which most of the chromium compounds are obtained is *chrome iron ore*, $\text{Fe O, Cr}_2\text{O}_3$. Compounds of chromium are largely used, on account of their inherent colour, as pigments in painting and printing; they form also the chromogenous substance of chrome-yellow and chrome-orange in dyeing proper. As mordants they are of the highest value, and finally the bichromates are very important oxidising agents, both in the laboratory and in the arts—*e.g.*, in the manufacture of alizarin.

The formulæ of the derivatives of chromic oxide, like those of the aluminium compounds, are usually written with two atoms of chromium—*e.g.*, $\text{Cr}_2(\text{O H})_6$, instead of $\text{Cr}(\text{O H})_3$, and Cr_2Cl_6 , instead of CrCl_3 , because it was also believed that chromium was quadrivalent and acted as a hexavalent double atom, $\text{Cr}_2^{\text{VI}} = \equiv \text{Cr} - \text{Cr} \equiv$.

Chromium forms three different compounds with oxygen:—

1. Chromium monoxide, Cr O.
2. Chromic oxide, Cr_2O_3 .
3. Chromium trioxide, CrO_3 .

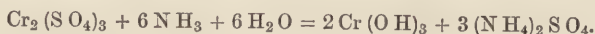
Chromium monoxide has scientific interest only.

Chromic Oxide or Chromium Sesquioxide, Cr_2O_3 .—Chromic oxide is contained in chrome iron ore, and is formed as a green

amorphous powder, or very dark green hexagonal crystals by heating chromic hydroxide; it is not readily soluble in acids.

Chromic oxide is used as a green pigment under the name of chrome-green.

Chromic Hydroxide, $\text{Cr}(\text{O H})_3$ or $\text{Cr}_2(\text{O H})_6$ —*Chromic Hydrate*; *Chromium Hydroxide*.—Chromic hydroxide is obtained by the addition of ammonia to solutions of chromium salts—



Caustic potash or soda and the alkaline carbonates act in the same manner; the carbonates form basic carbonate of chromium.

The normal colour of chromium hydroxide is green, and its composition is $\text{Cr}_2\text{O}_3 + 5 \text{H}_2\text{O}$, or $\text{Cr}(\text{O H})_3 + \text{H}_2\text{O}$.* The chromic hydrates precipitated by a quantity of alkali insufficient to precipitate the whole amount present are always of a green colour; if the reagent is in excess, the precipitate is violet-blue. A violet precipitate can be transformed into a green through the loss of water. On adding ammonia to cold solutions of chromium salts, a dark green gelatinous substance is formed, while in precipitating boiling solutions a light green powder is obtained. By drying the precipitate at 100°C ., it becomes greyish-black, and has the constant composition, $\text{Cr}(\text{O H})_3 + \text{H}_2\text{O}$ or $\text{Cr}_2\text{O}_3 + 5 \text{H}_2\text{O}$.

Sugar, oxalic, citric, and tartaric acids more or less impede the precipitation, and sometimes redissolve the precipitates on standing, forming red solutions. The precipitate partly dissolves in an excess of ammonia, with a red colour; on boiling, the precipitation is complete. In caustic potash or soda, the precipitate dissolves with an emerald-green colour, but is completely thrown down by continued boiling, the supernatant liquor becoming decolorised. The solution is also precipitated by ammonium chloride. The hydroxide is but sparingly soluble in solutions of the alkaline carbonates. When precipitated in the presence of a magnesium compound, chromium hydroxide, like aluminium hydroxide, does not redissolve readily (see p. 218).

Chromium hydroxide, on being heated to 200°C . in a current of hydrogen, is changed to the *hydroxide*, $\text{Cr O}(\text{O H})$, and on further heating forms chromic oxide.

The fine pigment, *Guignet's green*, is the *chromium hydroxide*, $\text{Cr}_2\text{O}(\text{O H})_4$, and is obtained by melting potassium bichromate with boracic acid. It is insoluble in water, and but slowly affected by boiling acids.

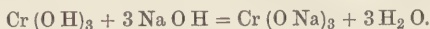
By dialysis of a solution of chromium hydroxide in chromium chloride, a *soluble chromium hydroxide* is formed, which contains for 66 equivalents of $\text{Cr}(\text{O H})_3$ one equivalent of H Cl (*Graham*).

Chromic hydroxide strongly resembles aluminium hydroxide. It

* Prudhomme, *Bull. Soc. Ind. Mulhouse*, 1889, p. 599; *Journ. Soc. Dyers and Col.*, 1890, p. 147.

forms *chromium salts* with acids, but acts towards caustic potash and soda as a very weak acid, forming therewith salts which are called *chromites*.

Chromites.—Potassium- and sodium-chromite are obtained by dissolving chromic hydroxide in 3 equivalents of caustic lye—



The alkaline chromites have not been prepared in the solid state. The affinity of the alkalies for chromium hydroxide is weaker than that which they evince for aluminium hydroxide. All acids (even carbon dioxide) and ammonium salts decompose the solutions of alkaline chromites. Moreover, these solutions are slowly dissociated, if free from an excess of caustic alkali. If a textile fibre is present the decomposition is effected more rapidly, owing apparently to the fibre, &c., exercising a catalytic action. In all cases chromic hydroxide is precipitated.

Chromic hydroxide in its alkaline solution has the curious property of dissolving other metallic oxides, such as the ferric and the cupric oxides. Ferric oxide dissolves readily, and the brown solution remains clear for weeks without any precipitate forming. The alkaline solution of chromic and cupric oxide is blue; on heating to incipient boiling, red cuprous oxide is precipitated and sodium chromate formed.

Chromium- or Chromic Salts.—The salts in which chromium acts as a base have a green or a violet colour. Some of them dissolve in water, and most of them in hydrochloric acid; those which are soluble in water have a disagreeable astringent taste and an acid reaction (as shown by their reddening blue litmus). The solutions have a fine dark-green or dark-violet colour; on heating them to over 65° C. the latter colour passes into the former, but returns, sooner or later, on cooling. Only the violet solutions yield crystalline salts, whereas the green solutions deposit amorphous compounds when evaporated. The former contain normal salts, while the latter are believed to be mixtures of acid and basic salts. The behaviour of the chromium salts to carbon dioxide, sulphuretted hydrogen and ammonium sulphide is like that of the aluminium salts. Their reactions with the alkalies have already been referred to in the description of the hydroxide. On the whole, the chromium salts are more stable than the aluminium salts and for this reason they are not so easily fixed on the cotton fibre as the latter.

Liechti and Schwitzer * found that normal chromium salts are not dissociated either by heat or by dilution with water. The basic chromium salts are less easily decomposed than the corresponding aluminium compounds, but the more readily, the greater the basicity

* *Journ. Soc. Chem. Ind.*, 1885, p. 586.

of the salt is. The quantity of chromium retained by the fibre during the consecutive processes of mordanting, drying, and ageing increases also with the basicity of the mordant; the strongly basic sulphates yield apparently the greatest quantity to the cotton fibre, but not as much as the aluminium mordants. The influence of other salts present in the mordanting solution appears doubtful in the light of Liechti and Schwitzer's experiments, which are somewhat discrepant. It seems, however, that such salts have an influence opposite to that which they exert on the aluminium salts—that is, they make the salts more stable. Freshly-prepared solutions of chromium salts resist dissociation more powerfully than those which have been kept for some time.

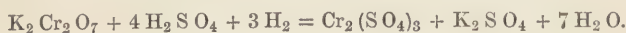
Chromium Sulphate, $\text{Cr}_2(\text{SO}_4)_3$.—This salt is obtained by dissolving chromium hydroxide in sulphuric acid; the solution, which is at first green, becomes blue after some weeks standing, and yields a crystalline greenish-blue mass. By repeated crystallisation from diluted alcohol, violet-blue regular octahedra ($\text{Cr}_2(\text{SO}_4)_3 + 15\text{H}_2\text{O}$) can be obtained. The ordinary solutions of chromium sulphate are either violet or green; the violet solutions become green when boiled. Barium chloride throws down all the sulphuric acid from the violet solutions at the ordinary temperature; but only by prolonged boiling from the green solutions. The solutions of chromium sulphate are precipitated on addition of caustic soda, ammonia, or the carbonates, phosphates, arsenates, and silicates of the alkalis. The precipitate dissolves in an excess of caustic soda, and in a great excess of ammonia, but is completely thrown down again on boiling. Basic chromium sulphates may be prepared by dissolving chromium hydroxide in the solutions of the normal sulphate, or of chrome-alum, or by the addition of sodium hydroxide, &c.

Unlike the corresponding aluminium compounds the basic chromium sulphates seem to be less liable to decomposition in the presence of sodium sulphate. The most basic salt that can be obtained by dissolving chromium hydroxide in chromium sulphate is that having the composition $\text{Cr}(\text{SO}_4)(\text{OH})$; whereas, by neutralising with sodium carbonate, the salt, $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$, is formed, which decomposes spontaneously after standing for three months. From chrome-alum (*i.e.*, in the presence of other sulphates) a still more basic salt, $\text{Cr}_2\text{SO}_4(\text{OH})_4$, can be prepared with sodium carbonate, but not with chromium hydroxide (see below).

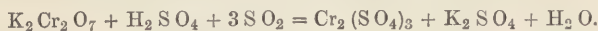
Normal chromium sulphate is not decomposed either on heating or on diluting with water, nor by the combined action of heat and dilution. The basic salts in concentrated solutions are not dissociated by boiling, but they are by diluting with water and by dilution and heat acting together. The more basic they are the more readily they are decomposed. The exact data as to dissociation can be seen from the table given in connection with chrome-alum.

Chromium sulphate is not used in the pure state, but as chrome-alum it is employed in the preparation of other chromium compounds.

Chrome-Alum, $\text{Cr}_2\text{K}_2(\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$.—This salt is obtained in great quantities as a bye-product in the manufacture of alizarin, in which case it contains, notwithstanding its beautiful crystallisation, a considerable amount of impurities, including calcium sulphate, tarry organic matter, and free sulphuric acid. The pure salt may be prepared by reducing potassium bichromate by means of starch, sugar, glycerin, alcohol, oxalic or sulphurous acid, or other reducing agents; the requisite amount of sulphuric acid must be added. The reaction is explained by the equation—



When sulphur dioxide is used, the reaction is as follows:—



For the preparation of pure chrome-alum dissolve

2 kgs. (2 lbs.) potassium bichromate in
10 litres (1 gall.) water, add
3 kgs. (3 lbs.) sulphuric acid,

heat to 35°C ., and add alcohol slowly, until a pure dark-green colour is obtained. The double salt, $\text{Cr}_2\text{K}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$, is obtained from the liquor by crystallisation.

Chrome-alum crystallises in large dark-violet octahedra, which dissolve with a violet colour in cold water. The solution becomes green on being heated to above 65°C . Chrome-alum is very soluble in water; 1 part of the salt dissolves in 7 parts of cold, and in 2 parts of hot water. It is insoluble in absolute alcohol.

Chrome-alum contains 39.3 per cent. of $\text{Cr}_2(\text{SO}_4)_3 = 15.3$ per cent. of Cr_2O_3 . The equivalent of the salt may, for all practical purposes, be considered to be 1000 instead of 998.6.

The behaviour of chrome-alum towards barium chloride is like that of chromium sulphate. The basic salts obtained from chrome-alum are less prone to dissociation than those prepared from the pure sulphate. The results obtained by Liechti and Schwitzer in their study of the dissociation of chromium sulphates, are stated in the following table. They worked with solutions equivalent to 225 grms. of crystallised chrome-alum per litre (*i.e.*, equivalent to 150 grms. of crystallised aluminium sulphate).

Cotton was mordanted with the solutions, and aged; the fifth column in the table shows the percentage of chromic oxide fixed thereby, calculated on the amount offered to the fibre by impregnating. The first column gives the composition of the sulphate; the second the mode of its preparation (from which the amount of potassium or sodium sulphate present can be seen); the third column states the relative dilution which effects dissociation; while the fourth shows the

degree of the dilution by which the salts are decomposed on boiling. As stated before, the normal or basic chromium sulphates are not dissociated (by boiling) in a solution of the indicated strength, either in the presence or absence of alkaline sulphates.

Table showing the dissociation of Chromium Salts in a solution equivalent to 225 grms. of crystallised Chrome-alum per litre :—

Composition.	Origin of Salt.	Dissociated by Cold Dilution.	Dissociated by Boiling Dilution.	Per cent. Cr_2O_3 retained by the Cotton Fibre.
1. $\text{Cr}_2(\text{SO}_4)_3$.	Pure sulphate.	Not dissociated.	Not dissociated.	12.8 per cent.
2. $\text{Cr}_2(\text{SO}_4)_3$.	Chrome-alum.	Do.,	Do.,	1.8 „
3. $\text{Cr}(\text{SO}_4)(\text{OH})$.	Pure sulphate and $\text{Cr}(\text{OH})_3$.	10 fold.	$\frac{1}{2}$ fold.	28.0 „
4. $\text{Cr}(\text{SO}_4)(\text{OH})$.	Pure sulphate and Na_2CO_3 .	$6\frac{1}{2}$ „	2 „	39.0 „
5. $\text{Cr}(\text{SO}_4)(\text{OH})$.	Chrome-alum and $\text{Cr}(\text{OH})_3$.	85 „	$10\frac{1}{2}$ „	29.7 „
6. $\text{Cr}(\text{SO}_4)(\text{OH})$.	Chrome-alum and Na_2CO_3 .	85 „	12 „	7.6 „
7. $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$.	Pure sulphate and Na_2CO_3 .	$1\frac{1}{4}$ „	0.4 „	86.4 „
8. $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$.	Chrome-alum and $\text{Cr}(\text{OH})_3$.	2 „	$\frac{1}{4}$ „	43.0 „
9. $\text{Cr}_4(\text{SO}_4)_2(\text{OH})_6$.	Chrome-alum and Na_2CO_3 .	16 „	2.6 „	22.6 „
10. $\text{Cr}_2(\text{SO}_4)(\text{OH})_4$.	Chrome-alum and Na_2CO_3 .	$1\frac{1}{2}$ „	$\frac{1}{2}$ „	87.5 „

On the whole, this table shows that a basic sulphate becomes more stable in solution with increasing amounts of alkaline sulphates, whereas with increase of basicity the sensitiveness of the sulphate towards dissociation becomes greater. Thus the salt $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$ cannot be obtained in a pure aqueous solution—i.e., by dissolving chromium hydroxide in a solution of pure chromium sulphate. Again, the salt $\text{Cr}_2(\text{SO}_4)(\text{OH})_4$ cannot be prepared at all with chromium hydroxide, neither from the pure chromium sulphate nor from chrome-alum. It must be made by means of chrome-alum and sodium carbonate, or by a process which shall supply the solution with a sufficient amount of the alkaline sulphate; this salt dissociates even when its solution is diluted with $1\frac{1}{2}$ volumes of water at the ordinary temperature. In the absence of alkaline sulphates the salt $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$ shows, practically, the same sensitiveness.

Chrome-alum is chiefly used for the preparation of other chromium compounds.

Chromium Chloride, CrCl_3 or Cr_2Cl_6 —*Chromic Chloride*.—Chromic chloride in the pure state is obtained as a sublimate, in beautiful violet crystals, by passing a current of chlorine gas over a red-hot mixture of chromic oxide and charcoal. These crystals do not dissolve readily in water unless a trace of chromium dichloride, CrCl_2 , be present. The solution yields green crystals of the composition $\text{CrCl}_3 + 6\text{H}_2\text{O}$, which are deliquescent in the air. By drying in the desiccator they form basic or oxychlorides, CrCl_2OH and $\text{CrCl}(\text{OH})_2$, and finally hydroxide, $\text{Cr}(\text{OH})_3$. On evaporating to dryness the solution gives rise to hydrochloric acid and basic chlorides.

The commercial article is obtained by the double decomposition of chrome-alum or chromium sulphate with calcium chloride, or by dissolving chromium hydrate in hydrochloric acid, and is sold as a dark-green solution. Another method of preparing chromium chloride is to heat bichromate, hydrochloric acid, and treacle or molasses in suitable proportions. It is doubtful whether a pure chloride is thus formed; the product probably contains some organic acid.

Basic chromic chloride, $\text{CrCl}(\text{OH})_2$, has been introduced by the Badische Anilin & Soda Fabrik as a mordant for cotton and silk. It is prepared by saturating a solution of chromic chloride with chromic hydroxide, or by using an excess of hydroxide and filtering. The mordant is used on cotton and silk like the basic aluminium-sulphates.

Chromium Fluoride, $\text{CrF}_3 + 4\text{H}_2\text{O}$.—This salt was introduced a few years ago by G. Stein. It comes into the market in the form of a green crystalline powder, which contains 42 per cent. of chromic oxide, Cr_2O_3 . The normal salt seems to be stable in aqueous solutions, and not to be dissociated by heating or diluting. It is very soluble in cold and hot water, and forms a green solution. Since it has a corroding action on glass and on most metals, it must be kept in wooden vessels, and leaden tubes should be used as steam pipes. Basic chromium fluorides (oxyfluorides) decompose on being evaporated, chromic hydroxide being separated. Chromium fluoride has been recommended as a mordant both for vegetable and animal fibres.* The value depends upon the non-injurious action of the liberated hydrofluoric acid upon fibres and colours. It is said to give better results in calico-printing than the chlorides and acetates, without affecting the fibre; and it is claimed that this salt can replace bichromate with advantage in wool dyeing, where the oxidising action of the latter is injurious—*e.g.*, for chroming indigo-dyed wool. A mordanting bath of chromium fluoride can be used continuously.

Chromium Nitrate, $\text{Cr}(\text{NO}_3)_3$ or $\text{Cr}_2(\text{NO}_3)_6$, is prepared by dissolving chromic hydroxide in nitric acid or by the double decomposi-

* G. Stein, *Journ. Soc. Dyers and Col.*, 1888, p. 60. H. Lange, *Journ. Soc. Dyers and Col.*, 1888, p. 73; 1891, p. 121.

tion of chrome-alum and lead acetate. By reducing bichromate in the presence of nitric instead of sulphuric acid, chromium nitrate is also produced. The salt crystallises with 9 molecules of water of crystallisation in purplish-red crystals, but these crystals are not easily obtained, as the solution generally yields an amorphous green mass. The article is sold as a blue solution which appears red by transmitted light; it is not extensively used. Basic salts are obtained from the solution by means of chromic hydroxide, soda, &c. Chromium nitrates behave in the same way as the corresponding sulphates and chlorides. Of the three kinds of salts the sulphates seem to be the most stable, next come the chlorides, and then the nitrates, the last being the most readily dissociated.

Chromium nitrates, normal and basic, serve as mordants for cotton. In former years they were employed to produce a light green shade on calico. The pieces were simply impregnated with the solution, and aged when the green colour of chromium hydroxide appeared (*Schuetzenberger*).

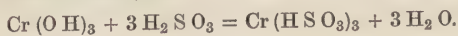
Chromium Chlorate, $\text{Cr}(\text{ClO}_3)_3$ or $\text{Cr}_2(\text{ClO}_3)_6$.—This salt may be prepared by the double decomposition of chrome-alum and barium chlorate. Its solution is violet or green, according to the temperature at which it has been prepared. A certain amount of barium sulphate always remains in solution, but is precipitated by boiling the solution or by adding hydrochloric acid.

Chlorate of chromium evolves a distinct odour of chlorine, and when heated to 100°C . it gives off large quantities of chlorine, and becomes transformed into a yellowish-red liquid containing chromic acid and oxygen compounds of chlorine. The solution decomposes after a few days.

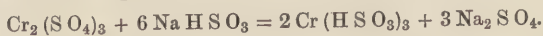
Chromium chlorate is a powerful oxidising agent. Prudhomme, who describes this salt (*l.c.*), has advantageously used a boiling solution of it for the purpose of making aniline-black ungreenable.

Basic chromium chlorate is used in calico-printing to produce steam catechu brown (*oxidation-mordant*).

Chromium Bisulphite, $\text{Cr}(\text{HSO}_3)_3$ (?).—If a current of sulphur dioxide is passed through water in which chromium hydroxide is suspended, a yellowish-green solution is obtained, which probably consists of chromium bisulphite.



The same compound is formed when a solution of a chromium salt is mixed with a bisulphite.



For the preparation of the substance a very strong solution of chrome-alum may be mixed with strong liquor of bisulphite of soda, until the bluish-green colour has changed to yellowish-green; an excess of bisulphite is advantageous. After a few days Glauber's salt crystal-

lises from the mixture. The solution, however, can be used immediately after being prepared.

Chromium bisulphite in solution yields on boiling a green precipitate which appears to be normal chromium sulphite, $\text{Cr}_2(\text{SO}_3)_3$, or a basic salt. Geuther gives it the formula, $\text{Cr}_4\text{S}_3\text{O}_{12} + 16\text{H}_2\text{O}$.

Prudhomme* states that the solution of chromium hydrate in sodium bisulphite liquor deposits after some time a green powder of chromium sulphite.

Chromium bisulphite decomposes on the fibre by steaming or drying, leaving chromium hydroxide; so that it is well adapted for mordanting cotton piece goods.

The pieces are padded in the solution, rolled up for two hours, and passed through Mather & Platt's steamer (see *Aniline-black*). Before padding the goods may be oiled. Instead of steaming they may be simply dried; but in this case they are very difficult to wet. After drying or steaming they are well washed in water, or in soda, if it is desirable to remove with certainty all sulphur dioxide from the fibre.†

Chromium Sulphocyanide or Thiocyanate, $\text{Cr}(\text{CN S})_3$ or $\text{Cr}_2(\text{CN S})_6$.—By dissolving chromium hydroxide in hydrosulphocyanic acid a green-violet solution is obtained, which yields a dark-green amorphous and deliquescent salt of the composition, $\text{Cr}(\text{CN S})_3$. The commercial article is prepared by the double decomposition of chrome-alum or chromium sulphate with barium or calcium sulphocyanide.

Basic sulphocyanides are obtained by adding chromium hydroxide, soda, &c., to the normal salt. They possess great stability; the most basic salt, $\text{Cr}_2(\text{CN S})(\text{OH})_6$, however, decomposes after some hours standing. Chromium sulphocyanide forms crystalline double salts with other sulphocyanides—e.g., potassium-chromium sulphocyanide, $\text{Cr}(\text{CN S})_3 + 3\text{K}(\text{CN S}) + 4\text{H}_2\text{O}$.

Solutions of the sulphocyanides do not dissociate either on heating or on diluting with water, except in the case of very dilute solutions of the more basic salts, which are decomposed on heating.

Sulphocyanides of chromium yield but small quantities of chromium to the cotton fibre by the operations of mordanting, drying, and ageing. If solutions equivalent to 225 grms. chrome-alum per litre are used, the cotton fibre retains, according to Liechti and Schwitzer, from—

The normal salt, . . .	$\text{Cr}_2(\text{CN S})_6$: 5.0 per cent.
The basic salt, . . .	$\text{Cr}_2(\text{CN S})_5(\text{OH})$: 8.9 "
" " . . .	$\text{Cr}_2(\text{CN S})_4(\text{OH})_2$: 14.4 "
" " . . .	$\text{Cr}_2(\text{CN S})_3(\text{OH})_3$: 20.9 "
" " . . .	$\text{Cr}_2(\text{CN S})_2(\text{OH})_4$: 33.7 "

* *Journ. Soc. Dyers and Col.*, 1890, p. 148.

† E. Kur, *Journ. Soc. Dyers and Col.*, 1890, p. 70.

of the available chromium. Comparison with chrome-alum shows that this is a much better cotton mordant than the sulphocyanide.*

Sulphocyanide of chromium is used by calico-printers for the production of steam logwood blacks. It behaves in the same way as the corresponding aluminium salt towards the fibre, not injuring the same.

Chromium Carbonate, $\text{Cr}_2(\text{C O}_3)_3$ (?), is obtained as a greyish-green powder when diluted solutions of chromium salts are precipitated at the ordinary temperature with sodium or ammonium carbonate.

Chromium Phosphates.—Chromium hydroxide dissolves in solution of phosphoric acid with a green colour. Phosphate of soda precipitates normal chromium phosphate, Cr P O_4 , from solutions of chromium salts as a green mass, which becomes dark blue on drying. This phosphate can also be obtained in the form of dark violet crystals, having the composition $\text{Cr P O}_4 + 6 \text{ H}_2 \text{ O}$. When chromium acetate is used, it is only produced by long continued boiling. The solution of chromium hydroxide in phosphoric acid yields, on evaporating and heating to 316° C ., a green chromium metaphosphate, $\text{Cr}(\text{P O}_3)_3$, which is insoluble in water and in acids.

Chromium Arsenite was formerly produced on the fibre as a self-colour of a light green shade; cotton piece goods were padded with a chromium salt and passed through a solution of arsenite of soda.

Chromium Acetate, $\text{Cr}(\text{C}_2 \text{ H}_3 \text{ O}_2)_3$ or $\text{Cr}_2(\text{C}_2 \text{ H}_3 \text{ O}_2)_6$.—Normal chromium acetate is prepared by dissolving chromium hydroxide in the requisite amount of acetic acid; or by the double decomposition of chrome-alum or chromium sulphate and lead acetate or calcium acetate. The salt has been obtained as hexagonal tablets, having the composition $\text{Cr}(\text{C}_2 \text{ H}_3 \text{ O}_2)_3 + \text{H}_2 \text{ O}$. The solution of chromium acetate is violet, and becomes greenish on being heated. It is not at all subject to dissociation; the salt can be evaporated to dryness and even heated without losing its solubility. The violet and green solutions of chromium acetate differ greatly in stability. The solutions are not readily precipitated at the ordinary temperature on addition of caustic alkalies, alkaline carbonates, phosphates and silicates, ammoniacal soap, or Turkey-red oil; but complete precipitation takes place on boiling the solutions with these additions for a longer or shorter period according to the degree of dilution; very long continued boiling is necessary if phosphate of soda is the precipitating agent.

Basic chromium acetates are prepared from the normal salt by the addition of chromium hydroxide, ammonia, caustic or carbonate of soda, &c., or by adding lead acetate or calcium acetate to basic sulphates. The violet solutions retain their violet colour on addition of basic agents, while the most basic salts prepared from violet

* Lauber (*Handbuch des Zeugdrucks*) states, on the contrary, that chromium sulphocyanide in print colours gives off the chromium with great ease and is an excellent mordant.

solutions are less sensitive to dissociation than the compounds similarly prepared from green solutions. This is in accordance with the supposition that the green solutions consist of mixtures of acid and basic salts; an addition of caustic soda, for example, would produce a more basic salt in a green solution than in a violet. Liechti and Schwitzer examined the chromium acetates for their dissociating and mordanting powers. They used solutions equivalent to 225 grms. chrome-alum per litre, which were prepared from normal sulphate or basic sulphate and lead acetate. Only the most basic salts were dissociated by heat alone. The normal salt and the first basic salt, $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_5(\text{OH})$, could not be decomposed by boiling, and the second basic salt, $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$, only by the combined action of a seventy-five-fold dilution and boiling. None of the salts were dissociated by simple dilution with water. On mordanting, drying, and ageing the cotton fibre retained of the available chromium

from the normal salt, $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_6$:	8.4 per cent.
„ basic „ $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_5(\text{OH})$:	25.7 „
„ „ „ $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$:	30.0 „
„ „ „ $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_3(\text{OH})_3$:	66.0 „
„ „ „ $\text{Cr}_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_4$:	69.9 „

Solutions of more basic acetates than these can be prepared. Chromium acetate (and chromium nitrate-acetate also) is not readily precipitated by sodium carbonate; on heating, only a precipitate is obtained; a cold solution of chromium acetate remains clear even when 3 equivalents of sodium carbonate (Na_2CO_3) are added for 2 equivalents of $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3$. Chromium acetates will dissolve lead sulphate in quantities increasing with the basicity of the chromium acetate; thus the addition of acetic acid to a basic salt precipitates the sulphate.

The great stability of chromium acetate somewhat prevents its application in cotton dyeing, while it is not used at all in wool or silk dyeing. It is, however, the most important chromium mordant for printing on cotton and woollen goods; the normal salt is employed. To prepare chromium acetate precipitate 1,000 parts of chrome-alum with 330 parts of soda ash (58°), filter, wash and press the precipitate, and dissolve it in 1,300 parts of acetic acid (30 per cent.). The solution may be concentrated by boiling; the usual strength is 32°Tw .

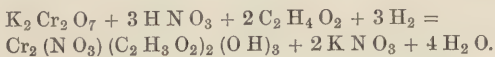
Chromium Sulphate-Acetates.—These salts are prepared, analogously to the corresponding aluminium salts, by decomposing chromium sulphate with an amount of lead acetate insufficient to effect complete decomposition, or by the addition of sodium acetate. By decomposing basic sulphates basic sulphate-acetates are obtained. In their general behaviour they resemble the chromium sulphates. Liechti and Schwitzer state that of the chromium

sulphate-acetates, neither the normal nor the basic is decomposed by dilution with water. The more basic salts only are dissociated by heat. The salt, $\text{Cr}_4(\text{SO}_4)(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_6$, yields on mordanting, drying, and ageing, 84 per cent. of the available chromium to the cotton fibre.

Chromium Chloride-Acetates are obtained by dissolving chromium oxychloride (basic chloride) in acetic acid, or by acting on a solution of chrome-alum with calcium chloride and calcium-acetate. The most basic salts only show signs of dissociation by the combined action of heat and dilution. The salt, $\text{Cr}_2\text{Cl}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_3$, yields to the cotton fibre on mordanting, &c., 50 per cent. of its chromium (*Liechti and Schwitzer*).

Chromium Nitrate-Acetates.—By evaporating a solution containing 5 equivalents of normal chromium-acetate and 1 equivalent of normal chromium-nitrate, a salt is obtained which crystallises in green tablets having the composition $\text{Cr}_2(\text{NO}_3)(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})$. By recrystallising this salt from strong acetic acid the salt $\text{Cr}_2(\text{NO}_3)(\text{C}_2\text{H}_3\text{O}_2)_5$ is formed.

Chromium nitrate-acetates are prepared by double decomposition of the sulphates with lead nitrate and lead-acetate. Another method, which is recommended by Witz,* is to reduce potassium bichromate with glycerin in the presence of nitric and acetic acids. The salt, $\text{Cr}_2(\text{NO}_3)(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_3$, is thus obtained, according to the equation—



3 kgs. (30 lbs.) crushed potassium bichromate,
4.4 litres (4½ gals.) boiling water, and
26 litres (26 gals.) nitric acid (66° Tw.)

are placed in an earthenware vessel standing in the open air; into this mixture are poured carefully

0.72 litre (3 quarts) white glycerin (48° Tw.), and
4 litres (4 gals.) acetic acid (30 per cent.),

half a litre (or 1 pint) at a time, constantly stirring with a long glass rod. When all the bichromate has dissolved, the mixture is rapidly brought to the boil in a copper boiler until a thin layer of the liquid appears of a fine green colour (about 2 minutes). An abundant crystallisation of saltpetre is obtained on cooling. The crystals are washed with water, and the washings are added to the green liquor. About 12.6 kgs. (126 lbs.) (50° Tw.) are obtained.

Chromium nitrate-acetates may also be prepared by simply mixing chromium nitrate and chromium-acetate in the requisite proportions. Basic salts are obtained by adding sodium carbonate or by mixing basic salts.

* A. Renard, "Traité des Matières Colorantes;" *Journ. Soc. Dyers and Col.*, 1885, p. 61.

Of the chromium nitrate-acetates the most basic only are dissociated by heat and by dilution. The salt, $\text{Cr}_2(\text{N O}_3)(\text{C}_2\text{H}_3\text{O}_2)_2(\text{O H})_3$, is decomposed by the action of heat on a very weak solution, and yields to the cotton fibre 48.5 per cent. of its chromium. The salt, $\text{Cr}_2(\text{N O}_3)(\text{C}_2\text{H}_3\text{O}_2)(\text{O H})_4$, is decomposed by heat alone, and deposits in the fibre by mordanting 69.1 per cent. of its chromium (*Liechti and Schwitzer*).

The chromium nitrate-acetates are employed as mordants in calico-printing.

Chromium Trioxide or **Chromic Anhydride**, Cr O_3 .—Chromium trioxide is obtained in the form of long ruby-red acicular crystals, by adding an excess of strong sulphuric acid to a concentrated solution of the bichromate.



The crystals are very soluble in water, with which they form a solution of chromic acid ($\text{H}_2\text{Cr O}_4$). Chromic acid is very easily reduced to chromic oxide, by reducing agents like sulphur dioxide, sulphuretted hydrogen, arsenic, and many organic substances; the reaction is so vehement that ignition sometimes occurs, as is, for instance, the case when alcohol is brought in contact with the dry crystals. Heated with nitric or sulphuric acids, chromium trioxide forms chromium salts and nascent oxygen; in the case of hydrochloric acid, chlorine is generated.

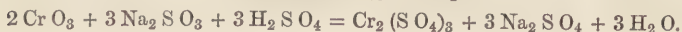
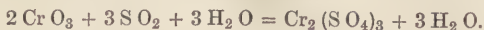


The aqueous solution of chromium trioxide is frequently used in the laboratory. The mixtures of bichromate and sulphuric acid, which are employed both as oxidising agents (*e.g.*, in the manufacture of alizarin) and as mordants, contain chromic acid.

In acid solutions the chromates are reduced in the same way as chromic acid, though less rapidly, by the action of oxidisable substances, and yield chromium salts; the reduction of chromates in alkaline solutions does not take place rapidly. Sulphuretted hydrogen is converted into sulphur and water—



Sulphur dioxide and sulphites yield chromium sulphate—



Potassium Chromate, $\text{K}_2\text{Cr O}_4$.—*Neutral* or *Yellow Potassium Chromate*, *Chromate of Potash*.—Potassium chromate is obtained by neutralising potassium bichromate with potassium hydroxide or carbonate. It forms yellow rhombic pyramids, which dissolve readily in water with a yellow colour, which is perceptible even in weak solutions. 100 parts of water dissolve about 60 parts of the salt at the ordinary, and less than 80 parts at the boiling, temperature.

Potassium chromate is readily converted by the action of acids into the bichromate. It is sometimes used in place of the bichromate.

Potassium Bichromate, $K_2Cr_2O_7$.—*Red Chromate* or *Bichromate of Potash*; *Bichrome* or *Chrome*.—Potassium bichromate is manufactured by heating chrome ironstone with lime and potash, when the chromium oxide is oxidised by the atmospheric oxygen, and chromates of calcium and potassium are formed.

Potassium bichromate crystallises in large orange triclinic prisms or tables, which are stable in the air and contain no water of crystallisation (in contrast with the sodium salt); it melts below red heat, and at higher temperatures it decomposes, forming oxygen, chromium oxide, and normal chromate. Its solubility in 100 parts of water is at—

0° C.	10° C.	40° C.	80° C.	100° C.
Parts.	Parts.	Parts.	Parts.	Parts.
5	8.5	29.2	73	102

Potassium bichromate has a cooling, bitter, and metallic taste. It is poisonous. The action of reducing agents on bichromate of potash has already been noticed.

Potassium bichromate, in presence of certain organic bodies, is affected in some way by the active rays of light. If a solution of the salt in gelatine is exposed to daylight, it becomes insoluble in water; those parts, however, which have not been so exposed remain soluble. This property is utilised in photography. The yellow colour of wool which has been mordanted with bichromate changes to green under the action of light, so that if the wool has not been completely exposed uneven dyeing will ensue. Judging from the green colour, a reduction of the chromic acid to chromic oxide has taken place.

Commercial potassium bichromate is almost chemically pure. It is the raw material for the production of all other chromium compounds (except in cases when the sodium salt is substituted for it), and is used in various industries—*e.g.*, in the manufacture of alizarin and the chrome colours (chrome-yellow, chrome-orange, Guignet's green). Dyers use bichromate very extensively. It is the most important wool mordant, while in cotton dyeing it is used in the production of aniline-black, cutch brown, chrome-yellow, &c.

Sodium Bichromate, $Na_2Cr_2O_7 + 2H_2O$.—This salt strongly resembles bichromate of potassium, except that it contains 2 molecules of water of crystallisation, is deliquescent, and is very easily soluble in water. It is, however, much cheaper than the potassium salt, and is produced in an analogous way. The commercial product is sold (1) in crystals containing 2 molecules = 12 per cent. of water

of crystallisation, or (2) in lumps or as a powder of the fused and partially dehydrated compound. The purity of the commercial product varies greatly; recently published analyses show 83·8 per cent. to 98·4 per cent. of pure anhydrous sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$).

Sodium bichromate crystallises in prisms or plates of the triclinic system which are of a yellowish-red colour, transparent and deliquescent. It has an acid reaction, and a bitter, cooling, metallic taste. It loses 1 equivalent of water below 75°C ., while all the water is given off below 100°C ., leaving the anhydrous salt as a light brown mass. It decomposes slightly above its melting point (320°C .) giving off oxygen; hence the fused products always contain some chromic oxide. When the crystals of the hydrated salt are dissolved in water, a considerable reduction of temperature occurs, while if the anhydrous be treated with water a rise in temperature is produced.

Arthur Stanley has published the following tables * of the solubility of anhydrous sodium bichromate in water and of the specific gravities of different aqueous solutions.

100 parts of water dissolve of sodium bichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) at

0°C .	15°C .	30°C .	50°C .	100°C .	139°C .
Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
107	109	127	143	163	210

The specific gravities of solutions of different strengths are the following:—

Per cent. $\text{Na}_2\text{Cr}_2\text{O}_7$	Specific Gravity.	Per cent. $\text{Na}_2\text{Cr}_2\text{O}_7$	Specific Gravity.	Per cent. $\text{Na}_2\text{Cr}_2\text{O}_7$	Specific Gravity.	Per cent. $\text{Na}_2\text{Cr}_2\text{O}_7$	Specific Gravity.	Per cent. $\text{Na}_2\text{Cr}_2\text{O}_7$	Specific Gravity.
1	1·007	11	1·078	21	1·147	31	1·216	41	1·287
2	1·014	12	1·085	22	1·153	32	1·224	42	1·294
3	1·021	13	1·092	23	1·159	33	1·231	43	1·300
4	1·028	14	1·099	24	1·165	34	1·238	44	1·307
5	1·035	15	1·105	25	1·171	35	1·245	45	1·313
6	1·042	16	1·113	26	1·178	36	1·252	46	1·319
7	1·049	17	1·120	27	1·185	37	1·259	47	1·325
8	1·057	18	1·127	28	1·193	38	1·266	48	1·330
9	1·064	19	1·134	29	1·201	39	1·273	49	1·336
10	1·071	20	1·141	30	1·208	40	1·280	50	1·343

Sodium bichromate in the form of crystals with 2 molecules of water is nearly equivalent to the (anhydrous) potassium bichromate, the mole-

* *Journ. Soc. Dyers and Col.*, 1886, p. 143.

cular weights of these two salts being 299 and 295 respectively; the equivalent of the anhydrous sodium salt is 263 in round numbers.

Sodium bichromate is used in place of potassium bichromate on account of its lower price and its greater solubility. It can, in nearly every case, replace the potassium salt perfectly. There is, however, some difference in the action of the two salts, as wool mordants, which has not yet been explained.

Barium Chromate (Ba Cr O_4) is obtained by precipitating the solution of a barium salt with chromate or bichromate of potash. It has a light yellow colour; is insoluble in water and in acetic acid, but soluble in nitric and hydrochloric acid; and is used as a yellow colouring matter under the name of "yellow ultramarine" in calico-printing. It offers the advantage that it is not blackened in an atmosphere containing sulphuretted hydrogen, but it does not give such full colours as chrome-yellow.

Lead Chromate (Pb Cr O_4) or *Chrome-Yellow*; and **Basic Lead Chromate** ($\text{Pb}_2 \text{Cr O}_5$) or *Chrome-Orange*. (See *Mineral colours*.)

Copper Chromates.—By the action of a concentrated solution of chromic acid on cupric hydroxide brownish-black deliquescent crystals of $\text{Cu Cr}_2 \text{O}_7 + 2 \text{H}_2 \text{O}$ are obtained. When the solution of this salt is boiled the basic salt, $\text{Cu}_3 \text{Cr O}_6 + 2 \text{H}_2 \text{O}$, separates out as a brown precipitate. The latter is also obtained by mixing boiling solutions of normal potassium chromate and blue vitriol, whereas cold solutions form the double salt, $\text{K}_2 \text{Cr O}_4 + \text{Cu}_3 \text{Cr}_2 \text{O}_9 + 2 \text{H}_2 \text{O}$.

Mixtures of potassium bichromate and copper sulphate are employed with good results for mordanting wool; the copper sulphate increasing the fastness of the colour.

Chromium Chromate, $\text{Cr}_2 (\text{Cr O}_4)_3$ (?).—By dissolving chromium hydroxide in chromic acid, and carefully evaporating and crystallising several times, needle-shaped crystals of a salt are obtained, which have the composition, $\text{Cr}_2 (\text{Cr O}_4)_3 + 9 \text{H}_2 \text{O}$.* Whether the same product is obtained by the double decomposition of chromium sulphate and chromate of potassium is not certain.

Basic Chromium Chromate, $\text{Cr}_2 (\text{Cr O}_4)_2 (\text{O H})_2$, may also be prepared by the action of chromic acid on chromium hydroxide. It dissociates rapidly in solution.

Basic Chromium Sulphate-Chromate, $\text{Cr}_2 (\text{S O}_4) (\text{Cr O}_4) (\text{O H})_2$, is obtained by dissolving 2 equivalents of chromium hydroxide, $\text{Cr} (\text{O H})_3$, in 1 equivalent of sulphuric acid and 1 equivalent of chromic acid—



The same compound is formed by double decomposition when 2 equivalents of $\text{Cr} (\text{O H})_3$ are dissolved in 2 equivalents of $\text{H}_2 \text{S O}_4$, and the product is acted upon by 1 equivalent of the normal chromate, or $\frac{1}{2}$ equivalent of bichromate of potassium or sodium.

* M. v. Gallois—German Patent, 45,999; English Patent, 1889, No. 376.—*Journ. Soc. Dyers and Col.*, 1889, p. 30.

The normal chromium chromate and the basic chromium sulphate-chromate are stable compounds in strong solutions. By boiling or by dilution with water they are dissociated, and the chromium hydroxide is precipitated in an insoluble form. The same effect is obtained by subjecting the salts in the fibre to the action of steaming, and by simply washing the fibre.

Under the name of chromium-mordants, G.A. I., G.A. II., and G.A. III., certain products are brought into the market by the Farbwerke, vorm. Meister Lucius & Brüning, which consist of chromium chromate or similar products. To the same class belong the mordants R.E. I., II., and III. for printing, which are issued by the same firm.

APPLICATION OF THE COMPOUNDS OF CHROMIUM TO THE TEXTILE FIBRES AS MORDANTS.

The salts of chromic acid are frequently employed in dyeing and printing. Chromic acid in the form of chromates or bichromates is also very extensively used as a mordant proper. It is, however, invariably the lower oxide of chromium—chromic oxide—which serves as the actual fixing agent, for, wherever chromic acid is employed as a mordant, it is reduced to chromic oxide before it forms the ultimate colour lake, either in the mordanting or in the dyeing process, or between these two in a separate operation. In certain cases the goods are treated with bichromate after the dyeing, and then chromic acid acts as an oxidising agent, and chromic oxide, which is generated thereby, takes the part of a mordant. The behaviour of chromic acid on “chromed wool” towards oxidisable dye-stuffs (such as logwood) is similar.

As the chromium salts and chromates are inseparable as mordants, they are here described together. The applications of chromic acid as an oxidising agent and as a dyestuff will be found in connection with the subjects where it acts as such (for instance, in the paragraphs on aniline-black and chrome-yellow).

Application to Cotton and Linen—(1) *Chromium Hydroxide in Alkaline Solution* (*H. Koechlin's Alkaline Chrome Mordant or Chromite of Soda*). *—Koechlin mixes 2 measures of chromium acetate (25° Tw.) with 2 measures of caustic soda (66° Tw.) and $\frac{1}{2}$ to 1 measure of water, then 1 measure of caustic soda lye in addition may be added to 5 measures of this mixture. If in the beginning only $1\frac{1}{2}$ measures caustic soda instead of 2 are used, the liquor becomes muddy and gelatinous.

Chromium acetate is obtained by precipitating 1000 parts of chrome-alum with 330 parts of soda ash (58°), washing the precipitate and dissolving it in acetic acid; the liquid is concentrated by boiling.

* *Journ. Soc. Dyers and Col.*, 1885, p. 18, and 1886, p. 25.

H. Schmid* saves the expense of acetic acid by dissolving the precipitate of chromic hydroxide, obtained from 1000 parts chrome-alum and 330 parts soda ash, in 50 parts (by weight) of caustic soda lye (50° Tw.) This alkaline mordant is not a stable product; after one or two days complete precipitation takes place; glycerin may delay this, but is liable to diminish the mordanting power. As the bath remains clear in the presence of a great excess of caustic soda, a known quantity of the latter is added to preserve the liquor, and this is neutralised with a corresponding amount of chromic hydroxide before the bath is used again. In all cases, however, only the requisite quantity of mordant should be prepared. The more caustic the bath the better it mordants; if insufficient soda is present, very little chromic hydroxide will precipitate, notwithstanding complete solution. On the other hand, too great causticity shrinks the fibre seriously by the action of mercerising.

A simplified method is the following:—

200 grms. (2 lbs.) chrome-alum,
1 litre (1 gall.) water, and
 $\frac{1}{2}$ litre ($\frac{1}{2}$ gall.) caustic soda (71° Tw.)

are mixed; the pieces are passed through this solution, beamed, and left for 24 hours, then passed through boiling water, washed, and dyed.†

Koechlin's alkaline mordant is one of the best chromium mordants for cotton which has been proposed. Unfortunately, it cannot well be used for yarns, on account of its caustic action on the hands of the workmen. Another disadvantage is that it cannot be used on oiled material, since the oil would be stripped from the fibre. Cotton piece goods are saturated with the cold liquor on the padding machine, rolled up and left for 12 hours, then washed, if possible, in running water. This mordanting process is not at all analogous to the fixation of alumina by means of aluminate of soda. The precipitation takes place by mere contact, and fixing agents are useless.

(2) *Chromium Salts as Mordants*.—It is difficult to impregnate the vegetable fibres with an amount of chromium salt sufficient to obtain a full shade. The sulphates, nitrates, acetates, nitrate-acetates, &c., have been employed with good results in calico-printing, but the demand for a good chromium mordant for the dyeing of cotton, especially of cotton yarns, has not been completely satisfied as yet.

Horace Koechlin has proposed the following method, which gives fairly good results:—The yarn is impregnated with the solution of a chromium salt, preferably a basic salt, dried and passed through a boiling solution of 1 part of soda ash in 10 parts of water; the operations are repeated if sufficient chromium has not been fixed. Chrome-alum, chromium sulphate, nitrate, chloride, acetate, nitrate-acetate,

* *Journ. Soc. Dyers and Col.*, 1886, p. 26.

† Private communication from M. Horace Koechlin.

&c., or their basic salts (like $\text{Cr}_4(\text{SO}_4)_3(\text{OH})_6$) are used; the acetates, and nitrate-acetates, yield less satisfactory results since they are not readily precipitated. It is essential that the soda solution be kept at the boiling temperature; since, otherwise, a smaller amount of the mordant will be fixed. Other salts, such as phosphate of soda, do not give such good results as sodium carbonate.

Better results are obtained if the fibre is prepared first with Turkey-red oil or tannin, or both, and, subsequently, with chromium salts. In this case the soda solution is replaced by cold water containing a small amount of lime, since soda would affect the organic mordant. The material is impregnated with 1 part of neutralised Turkey-red oil and 9 parts of water, or in the case of tannin being used it is steeped in a bath containing 1 part of sumach extract (52° Tw.) in 100 parts of water. The goods are entered into the bath at boiling temperature and allowed to soak 12 hours without further heating. Both processes may be combined by first oiling the goods and then preparing them with sumach. The material is simply wrung after these operations and passed into the chromium-mordant bath, where it is left for 2 to 4 hours; but when Turkey-red oil alone is used it is better to leave the goods over night in the chrome bath. After being wrung out the material is washed in water containing some lime, and is ready for dyeing. For full shades the various operations are repeated.

Chromium bisulphite is not suitable for the mordanting of yarns. Cotton piece goods are mordanted with this product in the padding-machine and left to lie beamed for 2 hours; they are then dried or, better, passed through the "Mather and Platt," and washed in water; it is not advisable to dry the material, because it is afterwards difficult to wet out.

The following instructions are given by the Hoechst Colour Works for the application of their chromium mordants, *G.A. I.* and *G.A. II.*, to cotton. Chromic acid seems to act simply as an acid like other acids in these preparations, and to exert no mordanting or oxidising effect. It should be remembered that these mordants are sensitive to light. The solutions of commercial strength do not dissociate.

Chromium Mordant, G.A. I. (M.L.B.), is recommended by the manufacturers for mordanting loose cotton, cotton yarn, and piece goods. It is a basic salt, containing chromium hydroxide, chromic acid, and hydrochloric acid.

The well-wetted material is steeped in the mordant, which has been diluted with water (1 to 4) for 12 to 24 hours, wrung out and carefully rinsed in water; or it is worked before rinsing, for 20 to 30 minutes, in a weak soda bath at 60° (1 part of soda ash in 200 of water). Alizarin-red and alizarin-brown require a stronger mordant (1 part of mordant to 2 parts of water). Piece goods are padded in a solution of 1 part of mordant and 2 to 4 parts of water, rolled up moist, left well covered up, and finally passed through a weak soda solution as before.

Chromium Mordant, G.A. II. (M.L.B.).—This mordant (which is also a basic salt containing chromium hydroxide, chromic acid, and acetic acid) is, according to the makers, specially adapted for the drying and steaming process, since after drying it is easily and completely fixed by a slight steaming. Instead of steaming, the material can be aged for 24 hours; on account of the sensitiveness of these mordants to light, the ageing must take place in a dark room.

For steaming 1 litre (1 gall.) of mordant *G.A. II.* is diluted with 4 litres (4 galls.) of water and 80 to 100 cc. (1 pint) of glycerin is added. The pieces are padded with this solution, dried and steamed for 10 to 20 minutes, without pressure, and fixed as stated before.

Mordant *G.A. II.* can also be applied by printing.

(3) *Bichromates as Chromium Mordants.*—Bichromate has been employed for mordanting cotton by being incorporated with the fibre, and subsequently reduced with some oxidisable salt by steaming. For yarns the processes are not practicable. H. Koechlin* has proposed the following method, which was for a long while unrivalled:—

800 grms. (8 lbs.) potassium bichromate, and
600 cc. (5 pints) ammonia are dissolved in
2 litres (2 galls) water;
800 grms (8 lbs.) hyposulphite of soda,
 $\frac{1}{2}$ litre ($\frac{1}{2}$ gall.) magnesium acetate (52° Tw.), and
4 litres (4 galls.) tragacanth thickening (60 to 1000)

are added. The pieces are padded with the resulting mixture, dried, and steamed for $1\frac{1}{2}$ to 2 hours, thus fixing chromic oxide and magnesia on the goods in the form of a very active and fast mordant, yielding a double lake. Hyposulphite is replaced with advantage by sodium or ammonium sulphocyanide, since this salt prevents a tendering of the fibre. The various salts have no action on each other at the ordinary temperature, if the light is excluded; but the bichromate is reduced under the influence of steaming in the presence of magnesium acetate by the hyposulphite or sulphocyanide, and chromic oxide is deposited in the fibre. This process requires a long continued and strong steaming, and, in consequence of the formation of oxycellulose, owing to the reduction of the chromic acid, often causes a tendering of the goods.

Another method, patented by E. Knecht, the principle of which was proposed by Prudhomme, is to reduce a chromate with a sulphite. H. Koechlin has indicated the following mode of procedure:—50 grms. ($\frac{1}{2}$ lb.) potassium bichromate, 100 grms. (1 lb.) bisulphite of soda (56° Tw.), and 100 grms. (1 lb.) ammonia are made up to 1 litre (1 gall.). The ammonia and bisulphite are first mixed, and then added to the solution of the bichromate. The mixture, which contains a large excess of ammonia, does not deposit any sediment; but if the ammonia is driven off by boiling or is allowed to evaporate, the

* *Journ. Soc. Dyers and Col.*, 1885, p. 25.

chromate is at once reduced and chromic hydrate formed. Cotton piece goods are impregnated with the solution, dried, and steamed; the process yields good results without any tendering of the fibre taking place.

Max Becke * has published a very interesting method, and claims to have obtained good results on the large scale. The principle of the method is to reduce chromic acid in the presence of the fibre by means of aniline. A more or less dark shade of aniline-grey is thus fixed along with a certain proportion of chromic oxide. The cotton prepared in this manner can subsequently be dyed with colouring matters which possess affinity for chromic oxide. For 100 parts of material there are used 2 parts of aniline hydrochloride, 16 parts of potassium bichromate, 4 parts of hydrochloric acid (34° Tw.), or an equivalent amount of sulphuric acid and 2,000 parts of water. Hydrochloric acid gives a yellowish-grey and sulphuric acid a bluish-grey. The operation is conducted in the cold for one hour, and the temperature raised to the boiling point by the end of the second hour and so maintained for half an hour. The material is then taken out and washed, when it is ready for dyeing.

J. J. Hummel has suggested that the vegetable fibre should be mordanted with tannin and subsequently treated with a boiling solution of bichromate. We find that up to 20 per cent. tannic acid or a corresponding quantity of sumach, &c., are necessary for full shades; the bichrome bath is prepared with 1 part of sulphuric acid for 3 parts of bichromate. In a similar way goods which have been dyed with cutch and developed in bichrome are practically mordanted with chrome, and may subsequently be topped with mordant dyes, like logwood, fustic, alizarin, &c.

According to another process proposed by E. Knecht, cotton yarn may be mordanted with chromium in the following manner:—It is first mordanted with tannin, passed through boiling chromium acetate 2° Tw., when it assumes a fine lilac colour. In order now to increase the amount of chromium fixed on the fibre, the yarn is passed through boiling bichromate of potash (5 grms. per litre), when the lilac colour turns to a brown, and this would appear to indicate the formation on the fibre of chromate of chromium.

Compounds of chromium are not used in *jute* dyeing, since this fibre is seldom dyed with mordant colours.

Application to Wool—(1) *Chromium Salts as Wool Mordants*.—Apart from chromium fluoride, which has only recently been introduced, chrome-alum is the only salt of chromic oxide that has been employed for wool-mordanting. The amount of chromium fixed from chrome-alum is about twice as great as that fixed by equivalent percentages of bichromate under the same conditions.† Probably a part of the chromium sulphate is simply absorbed by the wool fibre,

* *Journ. Soc. Dyers and Col.*, 1888, p. 24.

† Kay and Bastow, *Journ. Soc. Dyers and Col.*, 1887, p. 118.

and is not fixed in a permanent manner, since it yields in dyeing greatly inferior results to the bichromate. To obtain good and full shades with chrome-alum it is found necessary to use for each equivalent of chrome-alum from 12 to 18 equivalents of tartar.*

The salts of chromium have not been so thoroughly investigated as those of aluminium in their behaviour towards wool; we have seen, however, that they are considerably less easily dissociated; if, then, the hypothesis be correct that the wool fibre dissociates aluminium salts, and combines with the alumina, we may suppose that the wool does not readily dissociate chromium sulphate, and that it appropriates only a small amount of this mordant when the amount of tartar present is not excessive; this would account for the unsatisfactory results with chrome-alum.

Chromium fluoride has been frequently recommended of late, and it has been asserted that it would soon take the place of potassium bichromate in wool dyeing. At the present time the price of chromium fluoride is considerably higher than that of the bichromates; but this is compensated to some extent by its being applied more economically and requiring no tartar in the mordanting-bath. The value of this salt depends upon its easy, although not too rapid, fixation, and on the fact that it does not affect the feel and the spinning capacity of the wool fibre, even on prolonged boiling. It is of great advantage where it is desired to dye well through, and it seems particularly applicable where bichromate is injurious owing to its oxidising action. Comparative experiments† have shown that if a quantity of chromium fluoride, amounting to 1 per cent. of the weight of the wool, is used as a mordant, all the chromium is fixed on the fibre; while an equivalent quantity of potassium bichromate gives up only one-half of its available chromium. By employing as much of the chromium fluoride as amounts to 2 per cent. of the weight of the wool, 78 per cent. of the chromium is fixed, while about one-half of the bichromate remains in the mordanting liquor. In using 4 per cent. chromium fluoride nearly 70 per cent. is taken up by the fibre, whereas about 60 per cent. of the equivalent bichromate is left in the bath. The mordanting proceeds in a similar way as with bichromate; 4 per cent. chromium fluoride and 2 per cent. oxalic acid (of the weight of the wool) are used. The baths can be used continuously after being freshened up each time, care must be taken, however, that the amount of oxalic acid in the mordanting-bath does not become too large.

It has recently been recommended by the manufacturers of diamine fast red, anthracite black, and anthracene yellow to fix these dyestuffs on wool by first dyeing in an acid bath, and to mordant subsequently in the same bath with chromium fluoride (3 per cent.); colours fast to light and to milling are produced by this method.

* W. M. Gardner, *Journ. Soc. Dyers and Col.*, 1890, p. 37.

† *Journ. Soc. Dyers and Col.*, 1891, p. 121.

Wooden dye-vats with lead pipes for heating should be used for the application of the fluoride.

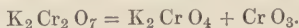
(2) *Chromic Acid as a Wool Mordant*.—Chromic acid in the form of bichromates of potassium and sodium is the most important and most generally used wool mordant; it offers the great advantages of being cheap and easily applied, as also of yielding full, brilliant, and fast colours. With a comparatively very small amount of the salt deep colours are obtained. The mordanting-bath is prepared with 2 to 4 per cent. potassium bichromate (of the weight of the wool) and the necessary quantity of water, amounting to from 50 to 100 times the weight of the wool. The wool is boiled for 1 to $1\frac{1}{2}$ hours with this liquor, and after being washed in water is ready for dyeing. Sulphuric acid (1 to 3 per cent. of the weight of the wool) is sometimes added to the bath either for the purpose of rendering the action of the mordant more energetic or of keeping the composition of the bath constant. For certain colours, *e.g.*, cloth red, the addition of sulphuric acid is necessary to obtain colours fast to milling. The wool which has been mordanted in this way with or without acid assumes a yellow colour and probably contains chromic acid. Under the influence of the active rays of light this colour is changed to green (see *Chromium Trioxide*); probably by reduction of the trioxide to chromic oxide. Goods which have been affected in this way are liable to dye unevenly and to have a speckled appearance. Passing through a bisulphite solution before dyeing may remedy this fault. More brilliant colours are obtained when organic acids or acid salts (for example, oxalic acid or tartar) are used along with the bichromate. The latter is partly reduced and chromic hydroxide formed on the fibre. In this case the wool has a greenish colour, like that of the chromium salts and chromic hydroxide. The quantity, however, of organic substances usually employed is very much less than would be required to reduce the whole amount of bichromate that is extracted from the bath by the fibre.

Another way of reducing the chromic acid is to pass the mordanted wool through a tepid solution of bisulphite of soda containing about 5 per cent. liquor (60° Tw.), calculated on the weight of the wool (*E. Knecht*). Treated in this manner the chrome becomes more completely reduced than if tartar had been used; and the results obtained in dyeing are much better with a large number of adjective dyes, notably logwood, alizarin-blue, coerulein, and gallein.

If a large excess of bichromate, especially in conjunction with sulphuric acid, is used, it exerts an injurious effect on some colouring matters by oxidising them and destroying their colouring principle, while at the same time the fibre is injured. Wool so treated is said to be "*overchromed*." Small amounts of bichromate do not exert this influence to so large an extent, but the products of oxidation diminish the brilliancy of the ultimate colour more or less. The reduction of

the bichromate previous to dyeing not only prevents this loss from overchroming, but also, by checking the decomposition of the colouring matter, allows of more brilliant shades being obtained.

R. L. Whiteley* boiled wool in a solution of potassium bichromate and then removed as much of the salt as could be extracted by repeated treatments with cold water for several weeks. The wool still contained a considerable quantity of chromic acid in some form, as was shown by the formation of chrome-yellow on the fibre when it was passed through the solution of a lead salt. Kay and Bastow (*l.c.*) found that in boiling wool with potassium bichromate the bichromate is decomposed and a certain amount of potassium chromate is found in the mordanting liquor. These facts indicate that the potassium bichromate is partly absorbed by the wool fibre and partly decomposed, its acid constituent being partly extracted and retained by the fibre as chromic acid, expressed by the equation—



Nietzki† has explained this fact by assuming that the chromic acid is partially reduced by the wool fibre to chromium chromate. Chromium chromate is but little known, and it is doubtful whether potassium bichromate in the absence of acids, or even normal potassium chromate would be reduced to any large extent in this way; whereas the normal salt has the same mordanting properties as bichromate, although much weaker. It is also improbable that under the conditions prevalent in the mordanting-bath—boiling temperature and great dilution—chromium chromate would be formed from chromium oxide and chromic acid, or that it could exist without dissociating. The mordanting properties of chromium chromate have not been examined yet; in Gallois' mordants (chromium mordants, G.A. I., II., III.) the chromium oxide is the only active mordant.

J. J. Hummel‡ says, if oxidation of the wool does take place, it is very slight, and, certainly, only a secondary accompaniment, not, by any means, the essential action, which accounts for the striking character of the mordanting powers of potassium bichromate.

E. Knecht,§ in view of the great affinity of wool for acids, argues that the mordanting of wool with bichromate is simply due to a dissociation of the salt into chromic acid (which combines with the substance, or a constituent of the substance, of the wool fibre) and the normal potassium chromate (which remains in the bath). During the dyeing, chromic acid is reduced partly by the dyestuff, partly by other substances present, and partly by the wool fibre, whereby it is converted into the mordant proper—chromium hydroxide. The fact that passing chromed wool through bisulphite solution does not give

* *Journ. Soc. Chem. Ind.*, 1887, p. 131.

† *Journ. Soc. Dyers and Col.*, 1889, p. 161.

‡ *Dyeing of Textile Fabrics*, p. 209.

§ *Journ. Soc. Dyers and Col.*, 1889, p. 186, *ib.*, 1888, p. 104.

the same results as mordanting with a chromic salt proves nothing, since this reduction takes place at the ordinary temperature, while it leaves the hydroxide mechanically precipitated, and the wool fibre shows little affinity for bases, especially in the cold. The mordanting with chromic salts, on the other hand, is effected at the boiling temperature, a compound of chromium hydroxide with the wool fibre being formed by dissociation, analogously to the mordanting of wool with aluminium salts.

E. Knecht (*l.c.*, 1889, p. 184) has compared the quantities of chromic acid which wool takes up under equal conditions from (1) neutral potassium chromate, (2) potassium bichromate, and (3) chromic acid (potassium bichromate mixed with one equivalent of sulphuric acid). He found that most was fixed from chromic acid and least from neutral chromate. Three pieces of flannel, each weighing 10 grms., were mordanted with these substances, in amounts equal to 3 per cent. of the bichromate (calculated on the weight of the cloth), and the amount of chromic acid retained by the fibre was estimated as chromic acid, as follows:—

From normal potassium chromate,	.	.	0.0605	gm.
„ potassium bichromate,	.	.	0.0805	„
„ bichromate and sulphuric acid,	.	.	0.1658	„

In mordanting with 3 per cent. bichromate (the amount usually employed on the large scale) only about 1 per cent. is fixed by the wool, as shown by experiments in the laboratory, and by analysing a series of mordant-liquors used in a dye-works. Usually dyers work their bichromate bath continuously, freshening up the same after each operation with a *greater* amount of bichromate than has been consumed. Analyses showed (*l.c.*) that the amount of bichromate remained almost constant at 0.5 gm. per litre when 3 per cent. bichromate was used the first time, and as much added after each operation; but the neutral chromate steadily increased up to an amount equivalent to at least 3.24 grms. of the bichromate per litre, when the bath had to be let off. A great quantity of chromium is thus lost every day, since the baths become overcharged with the salts, and have to be thrown away. Knecht therefore recommends that no more bichromate be added to the bath than is necessary to replace the amount extracted by the wool, as also that as much sulphuric acid be supplied as will reconvert most of the chromate into bichromate. Practical experience has shown that a chrome bath works better after it has been used two or three times than when fresh. This would indicate that it is best to have a mixture of normal chromate and bichromate in the bath, and that only so much acid should be added as will keep the liquor in this state.

Application to Silk.—For the mordanting of silk with chromium compounds normal or basic chromium salts are used. Bichromate does

not serve as a mordant proper, although it is used as an oxidising agent in the production of catechu brown.

Ungummed silk is steeped for 6 hours in a strong solution of a chromium salt (e.g., basic chromium chloride, 32° Tw.), wrung out, washed, worked in silicate of soda ($\frac{1}{2}$ ° Tw.) for 15 minutes, and again washed; it is then ready for dyeing.

Chromium Mordant, G. A. III.—(M. L. B.), is recommended by the makers for wool-printing and especially for dyeing the alizarin colours on silk. It consists of chromium chromate, $\text{Cr}_2(\text{CrO}_4)_3$.

Discharged silk is steeped for 12 to 24 hours in the mordant (1 part diluted with 4 parts water) and is ready for dyeing after simply washing with water.

IRON (*Ferrum*), Fe = 56.

Iron is bivalent in some compounds and tetravalent in others. Its specific gravity is 7.84. In pure air and in oxygen it does not tarnish. Pure water does not act on iron below red heat; but water containing carbonic acid and air oxidises it, forming rust or ferric hydroxide. Steam is decomposed by iron at red heat, magnetic oxide of iron being formed and hydrogen liberated. Iron is dissolved by most acids with evolution of hydrogen; but cold diluted nitric acid dissolves it without evolving gases, and forms ferrous nitrate and ammonium nitrate. With strong nitric acid the result is solution and conversion into ferric nitrate with evolution of nitrous gases; but if iron is treated for a short while with cold strong nitric acid and then washed with water, it becomes passive and is but slowly acted upon by chemical agents.

Iron forms four different compounds with oxygen:—

1. Ferrous Oxide, FeO .
2. Magnetic or Black Oxide of Iron, Fe_3O_4 .
3. Ferric Oxide or Sesquioxide of Iron, Fe_2O_3 .
4. Ferric Acid (Anhydride), FeO_3 .

Of these, the last named is known only in the form of some very unstable salts—e.g., potassium ferrate, K_2FeO_4 . This compound and the magnetic oxide are of no practical interest to dyers.

Ferrous Oxide, FeO , is a black powder which readily absorbs oxygen, passing into the higher oxides.

Ferrous Hydroxide or **Hydrate**, Fe(OH)_2 , is a white mass in the pure state; but greenish when slightly oxidised. The moist hydroxide absorbs oxygen with avidity, changing first to green and then to brown. It is a weak diacid base and is dissolved by acids with evolution of heat forming *ferrous salts*. Ferrous hydroxide is generated by the action of water containing air on iron. It dissolves in 150,000 parts of water, imparting to the latter an alkaline reaction and the peculiar taste of ferrous salts. Ferrous hydroxide is precipitated from

solutions of ferrous salts by caustic alkalies, but is not redissolved by an excess of the precipitant.

Ferric Oxide, Fe_2O_3 —*Sesquioxide of Iron*.—Iron sesquioxide occurs native in several minerals, and forms the red pigment *colcothar* or *caput mortuum*. It is obtained as a brownish-red powder by heating ferric hydroxide or a ferric salt of a volatile acid—*e.g.*, ferric sulphate. It dissolves slowly in acids. In ferric oxide, ferric hydroxide, and the ferric salts two tetravalent iron atoms are combined, and act as a hexavalent group $= \text{Fe} - \text{F} \equiv$.

Ferric Hydroxide or **Hydrate**, $\text{Fe}_2(\text{OH})_6$, is precipitated as a brown voluminous mass from the solutions of ferric salts by caustic alkalies. The precipitate becomes denser in boiling water, being transformed into the *hydroxides* $\text{Fe}_2\text{O}(\text{OH})_4$ and $\text{Fe}_2\text{O}_2(\text{OH})_2$. The precipitate is not redissolved by alkalies; but its formation may be prevented by organic substances such as glycerin. An alkaline solution of ferric hydroxide to which glycerin has been added has been proposed by H. Koechlin for the mordanting of cotton. The ordinary ferric hydroxide is not soluble in water; but under certain conditions it can be brought into solution by dialysis; it possesses no affinity to the textile fibres. Such dialysed iron is used in medicine, and may be employed as an antidote for arsenic poisoning internally and externally.

Ferric Hydroxide, $\text{Fe}_2(\text{OH})_6$, is a weak hexa-acid base. It does not form well defined salts with weak acids, but is readily soluble in most acids, forming with them *ferric salts*. Ferric hydroxide is soluble in neutral ferric salts, forming basic salts; and hence behaves like the aluminium and chromium hydroxides. These solutions when greatly diluted and heated are dissociated. Ferric hydroxide is slightly soluble in many organic substances, and imparts to them a yellowish to brown colour.

Ferrous Salts are white in the anhydrous state, but when they contain water they are greenish. They possess a sweet metallic taste, with an inky after-taste. Their aqueous solutions dissolve nitric oxide with a black colour. The soluble ferrous salts have an acid reaction. They are decomposed by strong heat. The caustic alkalies and lime precipitate ferrous hydroxide from the solutions.

Salts of ammonia prevent the precipitation by caustic ammonia completely, by other agents partially. The alkaline solution separates the ferric hydroxides in an insoluble state under the oxidising influence of the air. Organic substances, especially non-volatile acids and sugar, also impede the precipitation. Ammonium sulphide precipitates ferrous sulphide from neutral solutions of ferrous salts, and so does sulphuretted hydrogen from alkaline solutions.

The solutions of ferrous salts become turbid by absorbing oxygen from the atmosphere, forming basic ferric salts in the form of brownish flocculent precipitates. By other oxidising agents they are

also readily oxidised. With potassium ferrocyanide they give a white precipitate, which rapidly becomes blue on exposure to the air, but with potassium ferricyanide a blue precipitate (Turnbull's blue) is immediately formed

Ferric Salts.—Neutral ferric salts in the anhydrous state are nearly white; the hydrated neutral and the basic salts are yellow or reddish-brown. The aqueous solutions have a brownish-yellow colour, which turns reddish-yellow on heating. The soluble salts have an acid reaction, an astringent taste with an inky after-taste, and are decomposed on heating. Their solutions do not dissolve nitric oxide.

Ferric salts are obtained by the oxidation of ferrous salts with chlorine or nitric acid; and are easily reduced again, *e.g.*, by sulphuretted hydrogen, iron, stannous chloride, &c.

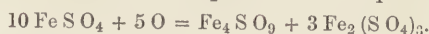
Caustic alkalies and their carbonates, lime, &c., precipitate from the solutions of ferric salts ferric hydroxide, which is not soluble in an excess of the precipitant, nor is it affected by the presence of ammonium salts. Organic substances impede the precipitation. Ammonium sulphide precipitates from the neutral, and sulphuretted hydrogen from the alkaline solutions of ferric salts ferrous sulphide.

Potassium ferrocyanide produces in solutions of ferric salts a beautiful blue precipitate, which is insoluble in hydrochloric acid, but is destroyed by caustic alkalies. Potassium ferricyanide colours the solutions of ferric salts a fuller red-brown *without producing a precipitate*; the formation of a blue precipitate in such solutions indicates the presence of ferrous salts. Potassium sulphocyanide produces in acid solutions of ferric salts a very intense blood-red colouration which does not disappear on heating with a little alcohol (test for presence of ferric salts in ferrous salts). In the presence of acetates, oxalates, or fluorides, much hydrochloric acid should be added to be sure of the test. The soluble ferric sulphocyanide can be extracted with ether, and this extract will show the colour still better. The test is an exceedingly delicate one with a freshly-prepared solution of potassium sulphocyanide.

Ferrous Sulphate, $\text{FeSO}_4 + 7\text{H}_2\text{O}$ —*Copperas; Green Vitriol.*—Ferrous sulphate is formed by dissolving iron in diluted sulphuric acid; it is prepared on the large scale from the iron pyrites or "dross" found in coal. The dross is exposed to the open air in clay-lined pits and the liquors which collect are boiled with scrap-iron in order to reduce the ferric sulphate to ferrous sulphate; they are then evaporated down in leaden pans and allowed to crystallise. It is also obtained as a bye-product in various manufactures. The commercial product forms bluish-green monoclinic crystals which effloresce in the air and become yellowish by oxidation. Ferrous sulphate is readily soluble in water, sparingly in dilute alcohol, but is insoluble in absolute alcohol and in concentrated sulphuric acid. 100 parts of water dissolve of the crystallised salt, $\text{FeSO}_4 + 7\text{H}_2\text{O}$, at—

10° C.	15° C.	25° C.	60° C.	100° C.	100° C.
Parts	Parts.	Parts.	Parts.	Parts.	Parts.
61	70	115	263	370	333

Solutions of ferrous sulphate do not dissociate either on heating, or on diluting; when oxidised by the air, however, insoluble basic ferric sulphates are precipitated, as exemplified in the equation:—



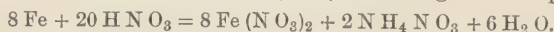
Basic ferrous sulphates cannot be prepared.

Ferrous sulphate should not contain any copper or alumina. Large crystals often contain free acid by enclosing some acid mother liquor. Ferrous sulphate is very extensively used in various industries. It is one of the most important and one of the oldest mordants known, and is still extensively employed, although it has been largely replaced in wool dyeing by chrome mordants.

Ferrous Chloride, FeCl_2 , or *Muriate of Iron*, is obtained by dissolving iron in hydrochloric acid, and is formed as a bye-product in the extracting of copper from spent oxide in the wet way. It forms deliquescent green crystals, having the composition, $\text{FeCl}_2 + 4 \text{ H}_2\text{O}$.

Ferrous chloride is used for the production of logwood black in wool-printing.

Ferrous Nitrate, $\text{Fe}(\text{NO}_3)_2$, is obtained by dissolving iron in cold diluted nitric acid (1.11 spec. grav.) according to the equation—



It is known in solution only, and is decomposed by gentle heat, generating nitric oxide and basic ferric salt. It can also be obtained by the double decomposition of ferrous sulphate and barium nitrate.

Ferrous Bisulphite, $\text{Fe}(\text{SO}_3\text{H})_2$ (?), has been prepared by mixing concentrated solutions of ferrous sulphate and sodium bisulphite. It has been recommended as a cotton mordant. The material is impregnated with the solution and steamed.

Ferrous Thiosulphate or **Hyposulphite**, FeS_2O_3 , has been recommended by E. Kopp for mordanting cotton goods, but has scarcely found practical application. The salt oxidises slowly on the fibre, forming first ferrous sulphate, and then changing to basic ferric sulphate. It is prepared by dissolving ferrous sulphide (FeS) in sulphurous acid, or by the double decomposition of ferrous sulphate and calcium thiosulphate, or by simply mixing solutions of ferrous sulphate and sodium thiosulphate (hyposulphite of soda).

A mixture of ferrous sulphite and ferrous thiosulphate is formed by dissolving iron in an aqueous solution of sulphurous acid.

Ferrous Carbonate, FeCO_3 , is formed on addition of sodium carbonate to the aqueous solution of ferrous salts. It dissolves in

water containing carbonic acid, forming an acid salt, the constituent of ferruginous mineral waters.

Ferrous Acetate, $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2 + 4\text{H}_2\text{O}$.—This salt is obtained by dissolving iron in acetic acid, or by the double decomposition of ferrous sulphate and lead or calcium acetate. It forms green monoclinic prisms containing four molecules of water of crystallisation, and oxidises rapidly in the air, forming basic ferric acetate. As the iron must be brought to the fibre in the ferrous state, and be fixed by oxidation, the ferrous acetate is too unstable to be used as a mordant. It is sometimes employed to produce iron buff on cotton. Impure solutions of ferrous acetates form the very important mordant next mentioned.

Pyrolignite of Iron—*Iron Liquor, Black Liquor*.—This product is obtained by dissolving scrap-iron in the so-called pyroligneous or crude acetic acid. It forms a dark olive-brown liquid of metallic taste and peculiar smell, and is made to stand at 20° to 30° Tw. The liquor can also be prepared by the double decomposition of ferrous sulphate and crude calcium acetate. Pyrolignite of iron consists principally of ferrous acetate, and contains a small amount of ferric acetate. It is generally supposed that the tarry matter from the crude acid prevents the oxidation of the ferrous salt. Moyret* has, however, shown that the presence of pyrocatechin alone is sufficient to impart all the characteristic properties—colour and stability—to ferrous acetate. Pyrocatechin and its methyl ether, guaiacol, are always present in pyroligneous acid, being products of the destructive distillation of cellulose (wood).

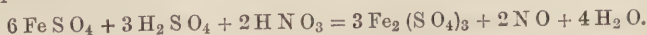
Pyrolignite of iron is used in cotton dyeing, in greater quantities in calico-printing, and in black silk dyeing.

It may contain as impurities an excess of acetic acid, ferrous and ferric sulphate, calcium and lead acetate. It is best to estimate the value of the mordant by a comparative dye trial.

Ferrous Oxalate, $\text{FeC}_2\text{O}_4 + 2\text{H}_2\text{O}$, is a crystalline lemon-yellow powder, almost insoluble in water. It is formed on mixing concentrated solutions of oxalic acid and of ferrous sulphate.

Ferrous Tartrate, $\text{FeC}_4\text{H}_4\text{O}_6$, is little known. It is only slightly soluble in water. By the action of tartar on iron filings ferrous potassium tartrate is obtained.

Ferric Sulphate, $\text{Fe}_2(\text{SO}_4)_3$, is obtained by adding nitric acid to a hot solution of ferrous sulphate, which contains the requisite amount of sulphuric acid—



The yellowish-brown solution yields on evaporation a syrupy liquid which deposits on standing small crystals containing water of crystallisation. Sulphuric acid precipitates from the concentrated solution

* *Teinture des soies*, Lyon, 1878, p. 197.

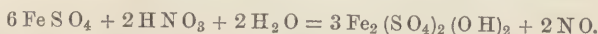
anhydrous salt. The anhydrous salt dissolves but slowly in water; at higher temperatures it is split up into ferric oxide and sulphuric anhydride.

By boiling the diluted solution or by incomplete precipitation with alkalis, basic ferric sulphates are thrown down; the same products are formed by oxidation when ferrous sulphate is exposed to the air. A solution of ferrous sulphate yields on oxidation with nitric acid red crystals of the composition $\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 + 14\text{H}_2\text{O}$. On dissolving in water they dissociate, forming an insoluble precipitate, $\text{Fe}_2(\text{SO}_4)(\text{OH})_4 + 5\text{H}_2\text{O}$. Soluble basic ferric sulphates are obtained by addition of sodium hydroxide to a solution of the normal sulphate, *e.g.*, the salts $\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2$ and $\text{Fe}_4(\text{SO}_4)_3(\text{OH})_6$; they dissociate after some hours standing. Basic salts which are prepared by dissolving ferric hydroxide in solutions of the normal salt are more stable, but at the same time more expensive. The best way to prepare the basic ferric sulphates is to oxidise ferrous sulphate with a quantity of sulphuric and nitric acid insufficient to form the normal salt. (See below.)

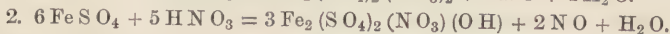
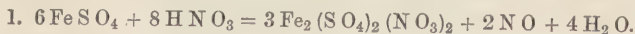
Ferric sulphate is the chief constituent of commercial "nitrate of iron."

"Nitrate of Iron" (*Rouille*).—In cotton and silk dyeing a liquor which is called *nitrate of iron* is very extensively used. It is prepared by heating a solution of ferrous sulphate with nitric acid and sulphuric acid, and consists of ferric sulphate, basic ferric sulphates, and ferric sulphate-nitrates. It does not contain, however, ferric nitrate or ferrous nitrate; hence the name "nitrate of iron" is a misnomer.

Normal ferric sulphate is obtained by the action of nitric and sulphuric acid on ferrous sulphate according to the equation which has been stated above. If a smaller quantity of sulphuric acid or none at all is added basic ferric sulphates are obtained, for example:—



Normal and basic ferric sulphate-nitrates are produced when the quantity of nitric acid is increased, as shown by the equations:—



Basic salts can also be prepared by adding caustic soda to the solutions of normal "nitrate of iron;" they dissociate, however, after a few hours; hence the product should be prepared from the beginning as basic as required by using the corresponding quantities of acids. Basic salts which have been prepared by dissolving ferric hydroxide in nitrate of iron are more stable than those obtained with caustic soda; but they are too expensive.

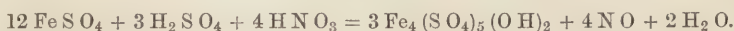
Liechti and Suida* have examined a number of commercial brands of nitrate of iron and prepared the following compounds:—

* *Journ. Soc. Dyers and Col.*, 1885, p. 60.

1. $\text{Fe}_4(\text{S O}_4)_5(\text{O H})_2$.
2. $\text{Fe}_2(\text{S O}_4)_2(\text{O H})_2$.
3. $\text{Fe}_2(\text{S O}_4)_2(\text{N O}_3)(\text{O H})$.

Most of the commercial products were found to correspond to the first formula, which was also found to be the best for silk dyeing by Moyret (*l.c.*, p. 203). One mordant which gives excellent results and is largely used in Crefeld is intermediate between the normal salt $\text{Fe}_2(\text{S O}_4)_3$ and that represented by formula No. 1. It nearly corresponds to the composition $\text{Fe}_2(\text{S O}_4)_{2\frac{7}{10}}$, and contains 11·5 per cent. total iron (0·5 per cent. iron in the ferrous state) and 27·2 per cent. " S O_4 ."

The first compound can be produced according to the equation :—



This equation demands for 72 parts of ferrous sulphate 6·3 parts of sulphuric acid and 12·6 parts of nitric acid (67° Tw.) Moyret (*l.c.*, p. 205) gives in his book the following prescription which corresponds fairly to this equation :—

A large closed vessel (constructed of stone, cast-iron, or even wood) is provided with a wide tube for the escape of the nitrous gases and with openings for the introduction of the materials and for a mixer. For 100 parts of nitrate of iron (90° Tw.) 72 parts of ferrous sulphate are necessary, or somewhat more, if the crystals contain much mother liquor. The requisite amount of ferrous sulphate is brought into the vessel, and after this has been closed a mixture of 6 to 7 parts of sulphuric acid (168° Tw.) and 10 to 15 parts of nitric acid (67° Tw.) diluted with a little water are poured gradually on to the crystals and the mixture is stirred. A reaction sets in and nitrous gases are given off which can be condensed in *bombonnes*. The reaction is first allowed to proceed at the ordinary temperature, and after it has subsided it is completed by blowing steam in. When no more gases are given off the reaction is complete and the liquid is transferred to reservoirs to cool and to settle. The reaction must be well regulated that it may not become too violent, otherwise insoluble basic ferric sulphates are formed whereby loss is caused and the remaining solution will not become basic enough.

The product has a deep red colour, and should contain about 17 per cent. of ferric oxide and but very little ferrous salt or hydrochloric acid ; it should not give a precipitate with silver nitrate, and, when diluted with much water, should give only a blue colouration but no precipitate with red prussiate of potash. Ferric chloride dissociates very incompletely, and ferrous sulphate impedes the dissociation ; the same is the case with sodium sulphate, hence the presence of these salts is objectionable. The commercial products contain, as a rule, some nitric acid which has escaped decomposition. Products of the same composition vary often in their tinctorial properties, especially

for silk dyeing; and their value is best estimated by comparative dye-trials.

Ferric sulphate-nitrates are also sold under the name of nitrate of iron. The way to prepare them has been indicated above. In oxidising ferrous sulphate the sulphuric acid is partly or entirely replaced by nitric acid. The products are deep brownish-red solutions of varying composition, and frequently contain ferrous salt. In cotton dyeing an admixture of the latter salt is sometimes advantageous. The value is also determined by the results they give in experimental dyeing. The ferric sulphate-nitrates are used almost exclusively in cotton dyeing. On the whole, "nitrate of iron" brands which are used for cotton are slightly less basic than those made for silk dyeing.

Iron Alum or Potassium Ferric Sulphate, $\text{Fe}_2\text{K}_2(\text{SO}_4)_4 + 24\text{H}_2\text{O}$, forms light-violet octahedra, and is soluble in about five parts of cold water. It is analogous to ordinary alum and the other alums. Iron alum is not used to any great extent in dyeing.

Ferric Chloride, Fe_2Cl_6 , in the pure state is obtained by heating iron wire in a current of chlorine, or by passing a current of dry hydrogen chloride over heated ferric oxide. It forms black or greenish hexagonal tables, with a metallic lustre, is deliquescent, and very soluble in water, alcohol, and ether, and can be volatilised. A solution of ferric chloride is obtained by dissolving ferric hydroxide in hydrochloric acid, or by oxidising a solution of ferrous chloride with nitric acid, with the addition of the required amount of hydrochloric acid. The concentrated solution is dark brown and viscid. The aqueous solution dissociates on heating, and the dissociation point is lower the greater the dilution. If the solution is not too much diluted the normal chloride is regenerated on cooling.

Basic chlorides are obtained by several methods, and some are soluble while others are insoluble in water. By dissolving freshly precipitated ferric hydroxide in pure ferric chloride dark red solutions can be prepared which contain even more than 20 equivalents of hydroxide for 1 equivalent of chloride, and can be diluted or boiled without decomposition. Acids or salts, however, precipitate ferric hydroxide or oxychloride, which is soluble in pure water. On addition of caustic soda to ferric chloride, oxychlorides are obtained which are soluble in water, unless they are more basic than the salt $\text{Fe}_2\text{Cl}(\text{OH})_5$; even this compound dissociates after a few hours.

The ferric chlorides, both the normal and the basic, dissociate too slowly to be applicable in dyeing.

Ferric Nitrate, $\text{Fe}_2(\text{NO}_3)_6$.—*Nitrate of Iron*.—This salt is prepared by slowly dissolving iron in nitric acid. When a precipitate of insoluble basic ferric nitrate begins to form the reaction is complete, and no more iron is added. A brown-red liquor is obtained, the composition of which varies. Moyret gives the formula $\text{Fe}_2(\text{NO}_3)_5\text{OH}$. Ferric nitrate is sometimes employed in silk dyeing; it finds a limited

application in black dyeing and in producing iron-buff shades on cotton.

Ferric Sulphocyanide or Thiocyanate, $\text{Fe}_2(\text{CNS})_6$, is obtained as a blood-red solution by dissolving ferric hydroxide in sulphocyanic acid, or by the double decomposition of ferric salts and sulphocyanides.

Ferric Phosphates.—On addition of phosphate of soda to ferric salts, a yellowish-white precipitate of ferric phosphate, $\text{Fe}_2(\text{PO}_4)_2$, is obtained, which is soluble in diluted mineral acids, but insoluble in acetic acid. (The precipitation becomes complete on addition of sodium acetate.) On this reaction is based the fixation of iron mordants with phosphate of soda.

A solution of ferric pyrophosphate, $\text{Fe}_4(\text{P}_2\text{O}_7)_3$, in ammonia has been recommended by Persoz as a cotton mordant.

Ferric Arsenate.—Sodium arsenate produces in solutions of ferric salts a white precipitate of ferric arsenate, $\text{Fe}_2(\text{AsO}_4)_2$, which is insoluble in acetic acid, but soluble in ammonia with a brown-red colour. Arsenate of soda is used to fix iron mordants on cotton in alizarin dyeing.

Ferric Acetate, $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_6$, is obtained by the double decomposition of ferric sulphate and lead acetate, and forms dark red tablets containing 2 molecules of water of crystallisation. Basic salts can be prepared by addition of caustic soda to the solution of the normal salt. According to Liechti and Suida, the normal salt does not dissociate either on heating or diluting with water. The basic salts are dissociated by heat, and all the iron is thrown down on boiling. Increase in basicity, as a rule, lowers the dissociation point; in diluted solutions, however, the dissociation point of the salt, $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_5\text{OH}$, is raised, that of $\text{Fe}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$ remains unchanged, whereas that of the more basic salts is lowered. The basic acetates are not dissociated by mere dilution with water.

Ferric acetates were extensively used in former years for black-dyeing the best qualities of silk, but they seem to have been replaced completely by nitrate of iron.

Ferric Nitrate-Acetate is prepared in the following way, according to Moyret:—Iron turnings are dissolved in nitric acid until the whole becomes a pasty mass of insoluble basic ferric nitrate, and this mass is subsequently dissolved in hot acetic acid, leaving a slight excess of the basic nitrate undissolved. A deep red solution is obtained, which is employed for the black-dyeing of silk intended for plush, because the colour it yields is not affected by hot-pressing.

Ferric Oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3$, is soluble in water, with a green colour. The solution is partly reduced to ferrous oxalate with evolution of carbon dioxide, both by boiling and by the action of light.

Ferric Tartrate, $\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3$, is very little known.

Alkaline Iron Mordants (*Ferrites*).—Ferric hydroxide does not dissolve in caustic alkalies; the presence, however, of certain organic

substances, notably glycerin or glucose, in solutions of ferric salts prevents the precipitation of the ferric hydroxide by alkalies, and thus an alkaline solution of ferric hydroxide can be prepared, which readily dissociates. Koechlin* has recommended the following mixture for preparing cotton piece goods:—2 measures of nitrate of iron (76° Tw.); 2 measures of caustic soda (66° Tw.); and 1 measure of glycerin (48° Tw.)

Burgemeister proposed a ferrous hydroxide solution to be prepared by mixing 1 kg. (1 lb.) of ferrous sulphate, 60 litres (6 galls.) of caustic soda (70°), and 2 litres ($1\frac{1}{2}$ pints) of glycerin.

These alkaline mordants have hardly found practical application, since they are expensive, and their strong alkalinity is objectionable. An alkaline mixture has been used for a long time, according to S. Balanche, in an Alsatian print works, to produce buff-yellow shades on cloth for linings. 20 parts of nitrate of iron (80° Tw.), 60 parts of glycerin, and 20 parts of ammonia are mixed and suitably diluted. The goods are impregnated with the mixture, and exposed to the air, when the ammonia is volatilised, and insoluble ferric hydroxide remains in the fibre.

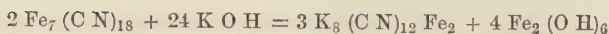
Prussian Blue.—By the reaction of ferrous and ferric salts with yellow and red prussiate of potash, several compounds are produced.

Yellow prussiate and ferrous salts produce together a white compound, which oxidises rapidly to form Prussian blue. The white compound probably has the composition $K_4Fe_2(CN)_{12}Fe_2$. Ferric salts produce in a solution of yellow prussiate which contains an excess of prussiate a blue precipitate of *ferric potassium ferrocyanide*, $K_2Fe_2(CN)_{12}Fe_2$. This substance, usually called *soluble Prussian blue* dissolves, when pure, in water with a blue colour, and is precipitated from the solution by salts.

Turnbull's blue or *ferrous ferricyanide*, $Fe_5(CN)_{12}$, or $(Fe_2)_2(Fe_2)_3(CN)_{24}$, is formed by precipitating ferrous sulphate with red prussiate, and, finally, *Williamson's blue* or *insoluble Prussian blue*, or *ferric ferrocyanide*, $Fe_7(CN)_{18}$ or $(Fe_2)_4(Fe_2)_3(CN)_{36}$, is obtained, together with soluble blue, when a solution of yellow prussiate is added to a solution of ferric chloride. The same compound is obtained by the action of chlorine or nitric acid on Turnbull's blue, or by precipitating the soluble Prussian blue with ferric chloride.

The *pigment Prussian blue* is prepared by precipitating a solution of copperas with yellow prussiate of potash and oxidising the white product with nitric acid. It forms an intensely blue powder or lumps having a coppery lustre, and consists of mixtures of the various blues. It is quite insoluble in water, but dissolves in ammonium tartrate with a violet, and in oxalic acid with a blue, colour. It is insoluble in the mineral acids and is not affected by them, but it is decomposed by alkalies with formation of ferric hydroxide and ferrocyanide; for instance:

* *Journ. Soc. Dyers and Col.*, 1885, p. 18; *ib.* 1885, p. 147.

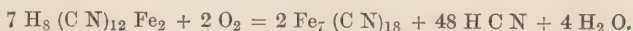


Hydroferrocyanic acid, $\text{H}_8 (\text{C N})_{12} \text{Fe}_2$ (or an acidulated solution of yellow prussiate), is dissociated on boiling; hydrocyanic acid escapes, while a white precipitate of an acid ferrous ferrocyanide is formed.



The same reaction is used for the preparation of hydrocyanic acid.

If an oxidising agent is present, *e.g.*, red prussiate, the reaction is somewhat different, and Williamson's blue is formed together with hydrocyanic acid:



Use is made of this reaction for the production of Prussian blue in wool dyeing and in calico-printing. In the latter case a mixture of yellow and red prussiate and tartaric acid is printed on the material and then steamed.

APPLICATION OF THE IRON SALTS TO THE TEXTILE FIBRES.

Iron salts are very extensively applied in dyeing and printing. Ferrous sulphate serves as a reducing agent in the preparation of the indigo-vat (lime and copperas vat); ferric oxide is precipitated in the fibres to produce iron-buff shades and Prussian blue; and sometimes ferric salts serve as oxidising agents—*e.g.*, to prevent aniline-black from turning green. The applications of iron salts in dyeing for mordanting purposes and for weighting silk which is to be dyed black are of great importance. This last operation cannot be considered a mere mordanting, since much more of the mordanting body is deposited in the silk fibre than would be required to obtain the desired shade, the intention being to increase the weight and bulk of the silk.

Application to Cotton and Linen.—(1) *Ferrous sulphate* or *copperas* is used in cotton dyeing. It is applied on tannin exactly like the ferric salt, and is also used similarly in the production of iron-buff shades. Sometimes it is used for darkening or "saddening" certain aniline colours which have been previously fixed with a tannin-mordant. In many cases the material (pieces) is first impregnated with a boiling decoction of a natural dyestuff or mixture of dyestuffs, such as logwood, fustic, peachwood, cutch, &c., and subsequently passed through a cold solution of ferrous sulphate.

Probably the commonest way of applying copperas in cotton dyeing (especially for blacks) is to prepare with tannin, pass through clear lime water, and then through the copperas solution. By the double decomposition of the calcium tannate and copperas, ferrous tannate is fixed on the fibre and calcium sulphate is formed, which is subsequently removed by washing. The ferrous tannate is rapidly oxidised in the air to ferric tannate.

Ferrous sulphate leaves only a very small quantity of iron on the fibre by mordanting and ageing, hence it cannot be advantageously applied by this method.

(2). *Ferrous Acetate* or *Pyrolignite of Iron* is not much employed in yarn dyeing, since for this material it offers no advantage over nitrate of iron, which is a cheaper article. It can be applied exactly like this product on goods previously mordanted with tannin. In the dyeing of cotton piece goods and in calico-printing it is very extensively used as a mordant in the production of blacks, purples, browns, &c. Ferrous acetate is applied exactly like aluminium acetate, by impregnating the fibre, drying, and ageing. But there is this difference, that the aluminium salt is merely fixed by the loss of acetic acid, whereas the iron salt loses acid and is oxidised to form a ferric compound. It is essential that the mordant be incorporated with the fibre in the ferrous state and be slowly oxidised while the acetic acid escapes, since ferric acetate cannot be fixed and is removed by the "dunging" bath. According to Schlumberger the best results in dyeing are obtained if the iron is in a state of oxidation intermediate between ferrous and ferric oxide. An energetic and rapid oxidation by passing through oxidising agents, like chloride of lime or bichromate, would not yield good results. The oxidation is regulated and restrained within definite limits by adding certain oxidisable substances to the mordant. A solution of white arsenic in acetic acid, to which some glycerin is added, is used for this purpose. Such a solution is called *purple fixing liquor*.

Pyrolignite is sometimes mixed with red liquor to obtain chocolate shades, and in this case a salt of copper is added to the fixing liquor. It is difficult to fix the mordant when printing a mixture of iron and aluminium pyrolignite. Oscar Scheurer* has explained this circumstance by the fact that red liquor generally contains sulphates which form ferrous sulphate by double decomposition. Ferrous sulphate is a bad mordant which leaves, on ageing, only a small amount of oxide on the fibre, whilst the same salt, with an addition of arsenic and a salt of copper, fixes much more. Scheurer has substituted, with good results, phosphoric acid for the arsenic.

The goods which have been mordanted with pyrolignite are passed, after ageing, through the dunging bath in the same way as those treated with red liquor; cow-dung, arsenate, phosphate, or silicate of soda, &c., are used; all give good results.

For logwood blacks on piece goods, a common method of applying pyrolignite of iron is to pad the pieces in the solution, dry at once on drying cylinders, and then pass through lime water.

(3). *Nitrate of Iron* is the iron mordant *par excellence* for cotton dyeing. A basic salt which holds an intermediate position between the normal salt, $\text{Fe}_2(\text{SO}_4)_3$, and the basic salt, $\text{Fe}_4(\text{SO}_4)_5(\text{OH})_2$, is

* *Journ. Soc. Dyers and Col.*, 1887, p. 193.

generally used. Basic ferric sulphate-nitrates of a similar composition are also frequently employed in cotton dyeing, as has been stated before.

The material may be mordanted by simply saturating it with nitrate of iron (3° to 6° Tw.), and subsequently passing it through a weak solution of caustic soda, soda ash, lime water, or chalk. The operations are repeated until enough ferric hydroxide is deposited in the fibre. In this way cotton is dyed iron-buff and blue (with prussiate). Another method is to prepare the material first with tannin (see this article), and subsequently work and soak it for 30 to 60 minutes in a cold bath of nitrate of iron (2° to 4° Tw.) In this way an insoluble ferric tannate is produced in the fibre. To facilitate the formation of the salt by double decomposition it is advisable to previously pass the goods, after mordanting with tannin, through clear lime water, whereby calcium tannate is formed and the formation of free acid in the iron liquor is prevented. A strongly caustic lye, however, would destroy the tannic acid. After the material has been steeped in the iron liquor it is washed well in water to which a small quantity of chalk is added with advantage, since it precipitates the ferric hydroxide more completely in the fibre and removes all free acid.

Goods which have been mordanted with ferric salts alone show a buff to brown colour; those mordanted with tannate of iron have a light brown or light grey to brownish-black or bluish-black appearance, the brown or blue being more decided according to whether the goods have been prepared with or without lime water. The dark colour prevents the application of iron mordant for light shades; in the production of dark colours tannate of iron serves partially as a mordant, partially as a self-colour, since it enables the dyer to produce full shades with relatively small amounts of colour.

Ferric Nitrate has a limited use in producing iron-buff and black shades. It is applied exactly like "nitrate of iron."

Jute is mordanted with copperas for blacks, the mordanting taking place after the impregnation with logwood extract.

Application to Wool.—*Ferrous sulphate* or *copperas* is practically the only iron salt which is used in wool dyeing. Half a century ago it was very extensively employed in dyeing logwood-blacks, but since that time it has been replaced almost completely by potassium or sodium bichromate. It is employed in conjunction with logwood for the production of cheap blacks, which are required to be fast to light, the logwood-blacks on chrome mordants being liable to turn green. (See *Logwood*).

More frequently ferrous sulphate is used nowadays for the fixation of wood colours to produce brown shades. It is principally applied by the so-called *stuffing and saddening* method, the wool being boiled first with a decoction of the dyewoods for about one hour, and after addition of 5 to 8 per cent. copperas for one half hour more; sometimes a certain amount of sumach is added to the decoction of the woods to

sadden the colour. Ferrous sulphate is also employed for darkening the shades of the alizarins and other mordant colours by being added to the exhausted dye-bath, and the boiling being continued for 15 to 30 minutes.

The application of ferrous sulphate is, by the *mordanting and dyeing* method, expensive, since comparatively large quantities of tartar, or oxalic acid, are required to produce good colours. With tartar in the mordanting-bath the wool receives a pale yellow colour, ferrous hydroxide probably being fixed by the fibre; without the addition of tartar a basic sulphate is precipitated in the fibre, which gives to the wool a deep reddish-brown colour.

For the production of Prussian blue on wool either yellow or red ferrocyanide of potassium, or a mixture of both, is used. (See under *Mineral Colours*.)

Application to Silk.—Iron salts are very important materials for the production of black silk, both for mordanting and for weighting the goods. (See *Black Dyeing of Silk* under the heading *Logwood*.)

Ferrous Sulphate is not extensively employed for this purpose. It is used in silk dyeing for the production of the so-called "English black" (*noir anglais*). (See *Black Dyeing of Silk*.)

Pyrolignite of Iron (*pied de fer*) is employed very extensively on raw silk, which has been previously prepared with tannin. The silk is first impregnated at 40° to 45° C. with a solution of tannic acid, generally in the form of chestnut extract; a quantity of extract standing at 15° Tw., equal to the weight of the silk, is used. After the silk has been saturated with tannic acid it is worked for a short time at 50° to 60° in a liquor of pyrolignite of iron (about 13° to 15° Tw.), wrung and exposed to the air for half an hour, again passed through the iron liquor, and hung up once more and finally rinsed well in running water. The silk absorbs by this treatment 30 per cent. of its own weight, and in most cases has not yet received the desired weight or colour. By the treatment with pyrolignite it has become capable of absorbing a fresh quantity of tannin matter, and is now mordanted again with chestnut extract as before, but half as much more extract is used. The silk loses in appearance by the second tanning (but this is restored later by the iron mordant), and the fibre swells up. After the second tanning the silk is rinsed in running water, and then mordanted again in pyrolignite as before. It has now acquired a good bluish-black shade, and has taken up altogether 70 per cent. of its own weight. The weighting can be increased by one or more repetitions of the mordanting with tannin and iron to 130 or 200 per cent. The quality of the water is of great importance; if hard water is used the weighting is much more effective than in soft water, which latter necessitates a more frequent repetition of the operations.

The silk, which has lost its lustre by these operations, is now worked in a softening bath consisting of 30 to 40 per cent. white soap

(of the weight of the silk) at the ordinary temperature, washed in running water, and then subjected to the brightening process. The brightening bath is prepared with sufficient hydrochloric acid to give a sour taste, and is used lukewarm. 6 to 12 per cent. of olive oil (in proportion to the weighting smaller or larger percentages) is added to the bath in a state of fine division, and the silk turned four to six times, wrung out, and dried at a low temperature. It has now regained its lustre, and acquired the peculiar crunching sound called the "scroop."

The pyrolignite bath is used continuously, and maintained at a strength of 13° to 15° Tw. by adding fresh liquor. The free acid which is liberated by the mordanting process is neutralised by adding iron filings to the bath and heating to incipient boiling; the scum which is formed thereby rises to the surface and is removed. The old method was always to have some iron filings in the bath, but a better plan is to hang a basket of iron filings in the upper part of the liquor from time to time, and to give the bath time to restore its neutrality by dissolving sufficient metal.

The bluish-black shade which the silk acquires by the treatment with ferrous salt cannot be obtained easily with ferric salts; oxidation seems to be an important factor, and if it proceeds too rapidly the colour is liable to be irregular.

For certain kinds of blacks a weak bath of pyrolignite is used between two tannin-baths for the sole purpose of improving the shade, not for weighting. (See *Black Dyeing of Silk*.)

Nitrate of Iron is used in enormous quantities for black dyeing and weighting of raw silk and boiled-off silk. Since silk which has been saturated with tannic acid becomes more or less impervious to ferric salts and in addition tannic acid would be destroyed by the oxidising action of ferric nitrate in the mordanting-bath, the treatment with nitrate of iron precedes the tanning. A basic salt of the composition $\text{Fe}_4(\text{SO}_4)_5(\text{OH})_2$ is most generally employed, as has been stated before, and this is readily dissociated, the silk attracting very considerable amounts of ferric hydroxide. Other ferric salts are employed in the same way. The mordanting of raw and boiled-off silk is essentially different.

Raw Silk is first worked in a tepid bath of sodium carbonate, washed and wrung out and then worked in a cold bath of nitrate of iron at 15° Tw. After half an hour to an hour it is wrung out, well rinsed in running water, steeped for 30 minutes in a soda bath (the temperature of which must not exceed 40° to 50°); and, finally, turned several times in cold water. This series of operations may be repeated two, three, or four times according to the depth of colour and the amount of weighting required.

Boiled-off Silk is mordanted in a much stronger bath of nitrate of iron, 52° Tw. being the usual strength. The material, which has been

well rinsed after being boiled-off, is worked for half an hour to an hour in the iron liquor, washed in running water, wrung out and worked for one hour in a boiling soap-bath to fix the ferric hydroxide. The soap-bath consists of boiled-off liquor to which are added 12 per cent. of olein soap and 2 per cent. of soda crystals (of the weight of the silk); it is essential that it should be actually boiling. The soap-bath is used continuously, the liquor from the silk being allowed to run back, and each time fresh additions of soap and soda are made; after each operation the bath is boiled up again in order that the iron soap formed may rise to the surface and be skimmed off. The silk which has been drained into the soap-bath is washed, first in a tepid soda solution, then in running water, and finally wrung. It has now acquired a brown colour, whereas it was pale yellow when it came from the iron liquor. The series of operations can now be repeated 7 to 8 times if necessary. As the silk is liable to be tendered by ferric salts on drying in the air, the material should not be allowed to dry when charged with the mordant; if it cannot be worked up directly, it is left in the mordanting-bath or well covered up with wet sheets.

The nitrate of iron baths are permanent, and the liquor which is drained from the silk is returned as completely as possible, since, in spite of the low price, the expense for nitrate of iron is considerable. The specific gravity of the baths is carefully maintained at the same degree by additions of fresh liquor.

Raw silk seems to possess a strong affinity for iron salts, since it takes up a large quantity from comparatively weak solutions; the subsequent rinsing in water completes the dissociation and removes the liberated acid salt before the basic salt is fixed by the soda-bath.

Boiled-off silk shows no affinity for the iron salts. The mordant is simply absorbed by the fibre and dissociated into a basic salt, which is precipitated in an insoluble state in the fibre, and an acid salt which is washed out; by systematic washing nearly all the iron salt can be removed, according to Moyret (*l.c.*) Hard water is much better for the washing of boiled-off silk in this phase of mordanting, since it fixes greater quantities of iron. Whereas the raw silk binds the mordant chemically, in the boiled-off silk it is simply deposited and liable to dissolve in the following iron liquor-baths. To prevent this it is subjected to the high temperature of the boiling soap-bath, whereby it is converted into a less soluble hydroxide; an iron soap is not formed in this case.

By each operation of mordanting with nitrate of iron the raw or discharged silk increases about 4 per cent. in weight; it acquires thus a deep brown colour and loses none of its lustre.

The washing of the mordanted silk is generally done with the aid of specially constructed washing machines. (See *Machinery.*)

The weighting of silk with ferric oxide for black-dyeing is fre-

quently followed by a treatment with ferrocyanide of potassium to produce Prussian blue. This treatment weights the silk still further ; but it also produces a dark navy-blue bottom which yields a fuller and finer black than can be otherwise obtained. In addition, the silk is better disposed to take up tannin-substances after the blue dyeing.

Raw silk and boiled-off silk are again treated in different ways, since they contain the oxide of iron forming the basis of the Prussian blue in a different state. Raw silk offers the oxide in a form which combines easily with the ferrocyanide, whereas the ferric oxide which has been precipitated by a hot soap-bath in the boiled-off silk is not easily affected and requires a higher temperature. About 10 to 20 per cent. of yellow prussiate of potash are used for each bath, in proportion to the weighting with oxide of iron which the silk has received previously ; an excess is not injurious. In addition a quantity of hydrochloric acid equal to the prussiate is required. An excess of acid may decompose the prussiate as is indicated by the intensely blue turbidity of the bath ; it is also injurious to the fibre, and the blue is not fixed well.

Raw silk is first placed in the bath which has been prepared with the prussiate and with about one-half of the hydrochloric acid required at 30° to 35° C. The silk is worked for half an hour in the bath and then lifted so as to allow of the rest of the acid being added, while the temperature is raised to 40°. The material is then replaced in the bath and worked as before, wrung out and washed in fresh water. It is then ready for the following dyeing and weighting operations, and has a blue, almost black colour, the depth of which depends on the quantity of ferric oxide already fixed.

Boiled-off silk is treated at a higher temperature in order to cause the ferric oxide to combine with the ferrocyanide ; otherwise the process is precisely similar. Enter at 30° C., turn the silk about ten times, heat to 45°, turn a few times, add the other half of the acid and heat to 50° to 55°, turn again a few times, wring out and wash well in water. The dyeing should take not less than 30 minutes ; the temperature may be carried to 60°, but not higher.

The baths of yellow prussiate are not used continuously—neither for raw nor for boiled-off silk. They are thrown out each time ; if the right quantities are employed they are nearly exhausted. In the same bath only such lots of silk should be dyed as have been prepared with nearly the same quantities of ferric oxide—*i.e.*, those which have passed through nearly the same number of mordanting operations.

TIN (*Stannum*), Sn = 118.1.

Tin is bi- and tetravalent. It forms a bluish-white metal of 7.3 sp. gr., which melts at 235°, and volatilises at a strong white heat. It is soft, malleable, and ductile, but not very tenacious, and

possesses a crystalline structure. Tin does not lose its lustre in the atmosphere; when heated strongly it takes fire and forms stannic oxide (Sn O_2). It dissolves in strong hydrochloric acid with evolution of hydrogen, forming stannous chloride (Sn Cl_2); the metal is attacked with great energy by strong nitric acid, nitrous gases being given off and stannic oxide formed. Tin is frequently employed, in consequence of its not being easily attacked, as a lining for dye-vats, especially in silk dyeing.

Tin combines in two proportions with oxygen to form

- (1) Stannous Oxide or Tin Monoxide (Sn O).
- (2) Stannic Oxide or Tin Binoxide (Sn O_2).

Stannous Oxide, Sn O , is a black powder that rapidly absorbs oxygen; it is prepared by heating stannous hydroxide in a current of carbon dioxide.

Stannous Hydroxide, Sn (O H)_2 , is obtained as a white powder on adding an alkaline carbonate to the solution of a stannous salt. It is soluble in caustic potash or caustic soda, not in ammonia. Stannous hydroxide is a weak base and a weak acid. The salts in which it acts as a base are called *stannous salts*, those in which it acts as an acid *stannites*. On boiling a solution of stannite of sodium tin is thrown down and sodium stannate formed; but if it is slowly evaporated, stannous oxide is deposited.

Stannous salts are produced by dissolving metallic tin or stannous hydroxide in acids; they are colourless, and are mostly decomposed by high temperatures. Those which are soluble in water reddens blue litmus and have a disagreeable metallic taste. They absorb oxygen from the air and are strong reducing agents. Sulphuretted hydrogen precipitates from the acid and neutral solutions dark brown stannous sulphide, which is soluble in caustic potash or soda and in the alkaline polysulphides.

Stannic Oxide, Sn O_2 , occurs native as tin stone, and can be prepared, by roasting tin, as a white powder, which is insoluble in acids and solutions of the alkalies; when melted with caustic soda it forms stannate of soda. Two *stannic hydroxides* of totally different properties are known,—*stannic hydroxide* or stannic acid and *metastannic acid*.

Stannic Hydroxide or Stannic Acid, $\text{H}_2\text{Sn O}_3$, is obtained as a white precipitate by adding ammonia to the solution of a stannic salt or an acid to a solution of stannate of soda. It is slightly soluble in water and reddens blue litmus; it dissolves readily in hydrochloric, nitric, and sulphuric acid, in caustic potash and caustic soda; it is both a weak acid and a weak base, the acid character being prevalent. The salts in which it acts as an acid are called *stannates*, the most important of which is stannate of soda (see p. 287). The soluble stannates have

a strong alkaline reaction, and are decomposed even by the carbonic acid of the air, stannic hydroxide being separated. The salts in which stannic hydroxide acts as a base are called *stannic salts*. They are colourless. Those which are soluble in water have an acid reaction, a disagreeable metallic taste, and are decomposed by strong heat. Sulphuretted hydrogen precipitates from acid and neutral solutions of stannic salts yellow stannic sulphide which is soluble in alkaline sulphides. Most of the neutral salts of the alkalies, notably sodium sulphate and ammonium nitrate, precipitate stannic hydroxide from the aqueous solutions, unless a great amount of acid be present in the free state.

Metastannic Acid, H_2SnO_3 (?) or $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ (?), is obtained by heating tin in concentrated nitric acid as a white powder, which is not readily soluble in acids or in alkalies. It is both a weak acid and a weak base. It is formed wherever tin is violently acted upon by nitric acid—*i.e.*, when the latter is too concentrated or the temperature employed too high. The formation of metastannic acid during the preparation of tin mordants is called “firing”; it must be avoided, since this substance has no mordanting power and its generation involves loss of tin.

Stannous Chloride, SnCl_2 —(**Tin Crystals** or **Tin Salt**, $\text{SnCl}_2 + 2\text{H}_2\text{O}$).—This salt is prepared by dissolving tin in hot hydrochloric acid; it forms in the anhydrous state a white transparent mass which melts at 250° and can be distilled without being decomposed. From the aqueous solution monoclinic crystals are obtained which contain two molecules of water of crystallisation ($\text{SnCl}_2 + 2\text{H}_2\text{O}$) and which are known commercially as *tin crystals*.

Stannous chloride in the crystalline form dissolves with absorption of heat and is soluble in 0.37 part of water. The clear solution becomes turbid on dilution with water, insoluble basic stannous chloride or oxychloride being separated by dissociation:—



The same precipitate is produced by the action of the air on the clear solution:—



Tin crystals are oxidised in the same way by the atmospheric oxygen. The basic chloride redissolves on addition of hydrochloric acid.

Stannous chloride dissolves readily in alcohol, and forms crystalline double salts with the alkaline chlorides. Solutions of stannous chloride which have been prepared by dissolving tin in hydrochloric acid without crystallising are sold under the names *single muriate of tin* and *double muriate of tin*, according to their lower or higher specific gravity (60°Tw. to 120°Tw.) Their composition varies; owing to an excess of acid they are less prone to dissociate than tin crystals.

Stannous Sulphate, SnSO_4 , is obtained by dissolving tin or stannous hydroxide in diluted sulphuric acid. The solution yields minute, granular, and very soluble crystals, and is dissociated by diluting with water.

Stannous Nitrate, $\text{Sn}(\text{NO}_3)_2$, is known in solution only. It is obtained by dissolving tin or stannous hydroxide in diluted nitric acid. In the former case ammonium nitrate is formed—



Stannous nitrate is usually prepared by dissolving tin in form of bars (grain bar tin)—not granulated tin—in eight times their weight of nitric acid (32°Tw.); the acid must be free from the lower oxides of nitrogen. Care is taken, by adding the tin bars slowly and keeping the acid cool, that no nitrous gases are given off; if the reaction becomes violent the mass is said to “fire,” metastannic acid being formed, which has no mordanting properties. The deep yellow solution of about 60°Tw. becomes turbid in the air, and deposits a white precipitate on long standing.

Woollen dyers use stannous nitrate in the production of cochineal scarlets under the names of *nitrate of tin*, *scarlet spirits*, *bowl spirits*.

Tin Spirits is a general term in the dyeing trade, given to a great variety of solutions of tin, in the preparation of which other acids besides hydrochloric acid, notably sulphuric, nitric, and oxalic acids, are used; along with these acids some salts, *e.g.*, nitrate of soda, salammoniac or common salt are employed, the utility of which often appears doubtful. They are chiefly used in wool dyeing in the production of certain colours with the natural colouring matters, and are largely prepared by the dyers themselves, who have their own peculiar recipes, on the virtue of which they believe their success depends. The value must be determined by a practical dye-trial (see also *Cotton Spirits*, p. 286). Since the introduction of the artificial dye-stuffs these tin spirits have lost their former importance.

Plum Spirit is prepared by dissolving tin in hydrochloric acid; some, however, also add nitric acid or sulphuric acid.

Yellow, Orange, Scarlet, Amaranth, Purple, Plum, Puce Spirit are all prepared by dissolving tin in mixtures of hydrochloric acid and sulphuric acid, or by adding sulphuric acid to “single” or “double muriate of tin.”

Nitro-muriate of Tin, Purple Spirit, Red Spirit, Aniline Spirit are mixtures of stannous chloride and stannous nitrate, prepared by dissolving tin in mixtures of the respective acids or in a mixture of “nitrate of tin” and hydrochloric acid. The tin is partly in the stannic state in these preparations.

Scarlet Finishing Spirit sometimes contains oxalic acid.

The difference in the value of these mixtures is greatly imaginary, and the better results which some dyers obtain with their peculiar

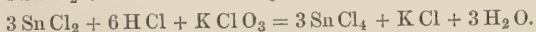
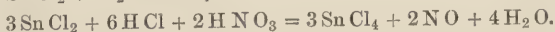
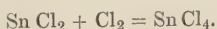
preparations are more due to the care and experience in making them than to the nature of the acids. The state of oxidation in which the tin is dissolved is of prime importance; for woollen dyeing the stannous salts are best, whereas in cotton and silk dyeing the stannic salts are chiefly employed.

Stannous Acetate, $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_2$, is prepared by the double decomposition of a solution of tin crystals, acidulated with acetic acid, and lead acetate. The colourless solution, which dissociates readily both on gentle heating and on diluting, is employed in calico-printing.

Stannous Oxalate, $\text{Sn C}_2\text{O}_4$, is obtained as a white crystalline powder on addition of oxalic acid to the solutions of stannous chloride. It is soluble in the solutions of alkaline oxalates, forming double salts. In mordanting wool with a mixture of stannous chloride and oxalic acid the precipitate which forms at first disappears. Under the name of *oxalate of tin*, mixtures of tin spirits containing oxalic acid are sometimes sold.

Stannous Tartrate, $\text{Sn}(\text{C}_4\text{H}_4\text{O}_6)$, has scarcely been studied. Stannous hydroxide is only sparingly soluble in tartaric acid, but dissolves easily in tartar. Stannous tartrate is rapidly dissociated by heat and by water; it is not a good wool mordant.

Stannic Chloride, Sn Cl_4 .—In the anhydrous state the salt is obtained by passing a current of chlorine gas over heated tin foil; it is a colourless liquid, which boils at 120° , and does not become solid at -29° . It fumes strongly in the air and combines with water, forming several crystalline hydrates which are very soluble in water— $\text{Sn Cl}_4 + 3\text{H}_2\text{O}$; $\text{Sn Cl}_4 + 5\text{H}_2\text{O}$; $\text{Sn Cl}_4 + 8\text{H}_2\text{O}$. Stannic chloride is prepared on the large scale by the oxidation of solutions of stannous chloride with chlorine gas or nitric acid, or chlorate of potash—



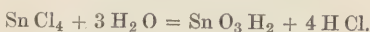
Tin crystals are dissolved, for example, in hydrochloric acid and boiling water, and potassium chlorate is added until the colourless solution becomes yellowish, and smells of chlorine. The reaction must not become too vehement, else insoluble metastannic acid is formed. For 1 kg. (10 lbs.) of dry crystals ($\text{Sn Cl}_2 + 2\text{H}_2\text{O}$) there are required about 1,300 grms. (13 lbs.) of hydrochloric acid (25°Tw.), $3\frac{1}{2}$ litres ($3\frac{1}{2}$ galls.) of boiling water, and 1,800 grms. (18 lbs.) of potassium chlorate. With a deficiency of hydrochloric acid the solution becomes turbid; if the slight excess of chlorine has not disappeared after the liquor has become cold, it is neutralised with a little stannous chloride. About 1,500 grms. (15 lbs.) of $\text{Sn Cl}_4 + 5\text{H}_2\text{O}$ are obtained; if an insufficient quantity of water is used crystals of a double salt of stannic chloride and potassium chloride will form. Large quantities of stannic

chloride are prepared by dissolving tin in aqua regia. Care must be taken not to allow the temperature to get too high.

Stannic chloride is sold in monoclinic crystals, $\text{Sn Cl}_4 + 5 \text{ H}_2 \text{ O}$, or as an aqueous solution. The following table gives the specific gravity and strength of solutions of pure stannic chloride ($\text{Sn Cl}_4 + 5 \text{ H}_2 \text{ O}$) at 15° , according to Gerlach:—

Specific Gravity.	Per cent. $\text{Sn Cl}_4 + 5 \text{ H}_2 \text{ O}$.	Specific Gravity.	Per cent. $\text{Sn Cl}_4 + 5 \text{ H}_2 \text{ O}$.	Specific Gravity.	Per cent. $\text{Sn Cl}_4 + 5 \text{ H}_2 \text{ O}$.
1·012	2	1·227	34	1·538	66
1·024	4	1·242	36	1·563	68
1·036	6	1·259	38	1·587	70
1·048	8	1·276	40	1·614	72
1·059	10	1·293	42	1·641	74
1·072	12	1·310	44	1·669	76
1·084	14	1·329	46	1·698	78
1·097	16	1·347	48	1·727	80
1·110	18	1·366	50	1·759	82
1·124	20	1·386	52	1·791	84
1·137	22	1·406	54	1·824	86
1·151	24	1·426	56	1·859	88
1·165	26	1·447	58	1·893	90
1·180	28	1·468	60	1·932	92
1·195	30	1·491	62	1·969	94
1·210	32	1·514	64	1·988	96

Diluted solutions of stannic chloride dissociate on long standing only; on boiling, stannic hydroxide is precipitated at once.



Stannic chloride combines with many chlorides, forming crystalline compounds—*e.g.*, $\text{Sn Cl}_4 + 2 \text{ S Cl}_4$ and $\text{Sn Cl}_4 + \text{P Cl}_5$. With the chlorides of the alkali metals it forms crystallised double salts.

Stannic chloride is an important mordant for cotton and silk.

Pink salt, $\text{Sn Cl}_4 + 2 \text{ N H}_4 \text{ Cl}$, is the double salt of stannic chloride and ammonium chloride. It crystallises from the solution of a mixture of the salts in small regular octahedra which are stable in the air and dissolve in 3 parts of water. The concentrated solution of the salt can be boiled without decomposition; the diluted solution separates stannic hydroxide on boiling.

Pink salt was largely used as a mordant in former years, but it has been replaced almost entirely by stannic chloride.

Stannic Nitrate and **Stannic Sulphate** have been but little studied. Stannic hydroxide dissolves both in nitric and in sulphuric acid. Stannic sulphate remains as a white mass on evaporating the aqueous solution; the solution of stannic nitrate coagulates at 50° .

Cotton Spirits or **Tin Spirits** are also general terms for solutions of tin salts used as mordants for cotton. We refer to what was said on p. 284. The cotton spirits consist chiefly of stannic salts, whereas the previously mentioned tin spirits are principally stannous salts.

There exists, however, a great amount of confusion as to the names. These preparations have also lost much of their importance since the introduction of the artificial dyestuffs. They are prepared by the dyers themselves in various ways so as to produce mixtures of stannous and stannic chloride and nitrate; for 1 to 2 parts of tin 8 to 16 parts of nitric acid and 8 to 50 parts of hydrochloric acid are employed; ammonium chloride, bichromate of potash, and other salts are also added.

Oxymuriate of Tin, Crimson, Burwood, Plum, Red Cotton, Purple Cotton Spirits, Solution of Tin, or simply "*Solution*" and *Pink Cutting Liquor* are some of the usual names.

Stannic Sulphocyanide or **Thiocyanate**, $\text{Sn}(\text{CNS})_4$, is obtained by the double decomposition of stannic oxalate (see below) and calcium sulphocyanide; or by dissolving stannic hydroxide in sulphuric acid and decomposing the solution with barium sulphocyanide. The diluted solution can be boiled without decomposition. Stannic sulphocyanide is used in calico-printing.

Stannic Acetate, $\text{Sn}(\text{C}_2\text{H}_3\text{O}_2)_4$, is obtained by mixing strong solutions of stannic chloride and sugar of lead with the addition of some acetic acid. The solution, which is used in the production of certain steam colours on calico, is not dissociated by boiling if it contains sufficient acetic acid—about one part acetic acid to two parts of crystallised acetate of lead is required.

Stannic Oxalate, $\text{Sn}(\text{C}_2\text{O}_4)_2$ —*Oxalate of tin*—is prepared by dissolving stannic hydroxide in a solution of oxalic acid on the water bath at 65° to 80° . The salt dissolves in much water; the solution becomes opalescent in the air.

Stannic oxalate is also used in calico-printing for the production of alizarin reds and similar colours.

Stannic Tartrate, $\text{Sn}(\text{C}_4\text{H}_4\text{O}_6)_2$.—Stannic hydroxide dissolves in a solution of tartaric acid. The compound has not yet been exactly described.

Sodium Stannate, Na_2SnO_3 —*Stannate of Soda; Preparing Salt*.—Sodium stannate is obtained by melting tin-stone (stannic oxide, SnO_2) with caustic soda or tin with sodium nitrate and caustic soda. The commercial product contains sodium chloride and carbonate; sodium arsenate and sodium tungstate are sometimes added to increase the effect of the salt.

Sodium stannate is a white crystalline mass, readily soluble in water. It forms crystals with 3 and 10 molecules of water. Stannic acid being a very weak acid, the salt has mild caustic properties. It is slowly decomposed by atmospheric carbon dioxide with formation of sodium carbonate and stannic acid, H_2SnO_3 . Sodium stannate is used in dyeing and in printing as a mordant. (See pp. 289 and 290.)

APPLICATION OF THE COMPOUNDS OF TIN TO THE TEXTILE FIBRES.

The compounds of tin are used by dyers almost exclusively as mordants. The colours they yield are distinguished, as a rule, by their brilliancy. Apart from their employment as mordants the stannic salts are used by silk-dyers for weighting white or light-coloured silk, and the stannous salts are employed in calico-printing as reserves and discharges. The stannous salts attract oxygen with great avidity, and their application in reserves and discharges is based on their reducing properties. The reducing power prohibits the stannous salt from being used in conjunction with oxidising mordants or with colouring matters which are decolorised by reducing agents.

Application to Cotton and Linen.—*Stannous Salts* are not frequently employed as mordants on cotton and linen. Persian berries yield a good yellow to orange shade on these materials previously mordanted with tannin and stannous chloride, and soluble blue is faster to light on material thus prepared than on tannin and antimony mordant. Certain lakes which are produced by means of stannous chloride and various extracts are sold under the name of *carmines*—e.g., Persian berry carmine, cochineal-carmine, &c., and are used in calico-printing. In Turkey-red dyeing stannous chloride is added in very small quantities to the clearing bath; whether it exerts in this case simply a reducing influence or enters into the colour lake as a mordant proper has not been decided.

Stannous chloride both reduces ferric salts and eventually converts them by double decomposition into chlorides, which do not readily dissociate and are not easily fixed on the fibre. For this reason stannous chloride is sometimes added to print colours, notably to alizarin reds, to preserve their brilliancy in the presence of ferruginous impurities.

Stannic salts are extensively used as mordants for cotton and linen. Many natural dyestuffs—e.g., logwood, fustic, quercitron, weld, barwood, &c.—are fixed on these fibres with stannic oxide. The cotton spirits which have been mentioned above are still used for this purpose, and were formerly employed in large quantities. Generally the material is first mordanted in tannin, then worked and soaked in a diluted liquor of stannic chloride or spirits, &c., and finally well washed before dyeing. In these cases tannic acid acts as a fixing agent for stannic hydroxide, which is the actual mordant. The inverse takes place with the aniline colours, which are also frequently dyed on tannic acid and stannic oxide, &c. (stannic tannate), the basic dyestuffs being bound to the fibre by tannic acid, while the stannic oxide simply serves to precipitate the tannic acid as an insoluble salt. An excess of tannic acid, if not converted into an insoluble salt, would

redissolve the ultimate colour lake (see p. 180). When tannin is thus fixed on cotton with stannic chloride in dyeing cotton and wool mixed goods the salt should be free from stannous salt, since the wool is liable to be mordanted by the latter.

Stannate of soda is employed as a mordant on the vegetable fibres for the same purposes as the stannic salts to fix the natural colouring matters, but it is applied differently on account of its opposite chemical character. The goods are simply impregnated with a solution of stannate of soda (4° to 10° Tw.) and then passed through very dilute sulphuric acid, or normal or basic sulphate of alumina. Stannic hydroxide, or in the latter case a mixture of stannic hydroxide and aluminium hydroxide, are precipitated in the fibre. This mordant also serves well for the eosins and for many azo-colours.

Cotton piece goods upon which steam colours are to be printed are sometimes prepared with stannate of soda and sulphuric acid, since brighter and richer colours are obtained in this way.

Application to Wool.—The tin mordant of the woollen dyer is principally stannous chloride, often in the form of the tin spirits already referred to. The best method is to mordant with about 4 per cent. stannous chloride, and 2 per cent. oxalic acid (of the weight of the wool) at the boil; tartar does not give such good results as oxalic acid. A mixture of equivalent amounts of stannous and stannic salt, as contained in many tin spirits, also gives good shades; it is, however, subject to deterioration. An excess of tin mordant makes the wool harsh and rough, and destroys its milling properties. The wool is entered into the cold mordanting-bath, the temperature gradually raised to boiling, and kept at this temperature for one hour. Oxalic acid first precipitates stannous oxalate, and the salt is slowly taken up by the fibre during the mordanting process.

Liechti and Schwitzer* have studied the behaviour of tin mordants towards wool. Stannous tartrate and stannic tartrate are not good mordants for wool, since they are too prone to dissociation. As is the case with aluminium, tin salts require an acid in the mordanting bath to prevent a premature dissociation and superficial fixing of the mordant. Stannous chloride and tartar give the best results in the proportions of 4 per cent. tin crystals and 3.2 per cent. tartar, *i.e.*, equal molecules. Better effects, however, are obtained by using 4 per cent. tin crystals and 2.1 per cent. oxalic acid (equal molecules), which mordant is besides preferable on account of its lower cost. Tartaric acid in the free state gives slightly better results than oxalic acid, but is not worth the greater expense involved by its use. A mixture of one equivalent of stannous and one equivalent of stannic salts gives very good results, and in this case oxalic acid is again the most satisfactory assistant; three equivalents or slightly greater quantities of the latter are required to obtain a colour fast to rubbing.

* *Journ. Soc. Dyers and Col.*, 1886, p. 177; 1887, pp. 25 and 44.

This mixed mordant has the disadvantage of deteriorating on standing for a long time.

In the case of mordanting with sulphate of aluminium and a tin salt it is best to employ stannous chloride along with tartar, according to Liechti and Schwitzer. Colours produced with this mordant have the advantage of not rubbing. According to the same authors, dyetrials with cochineal proved that in mordanting with stannous salts considerably more acid is taken up by the wool-fibre than with stannic salts. With some colouring matters no separate mordanting and dyeing is required, since the tin lakes which are formed at first are slowly taken up by the wool fibre. The dye-bath is prepared with the dyestuff, stannous chloride, and oxalic acid, tartar, &c., and the wool dyed by the so-called single-bath process.

Stannous chloride is added to the dye-bath in certain cases towards the end of the dyeing process to shade the colour by making it more brilliant; this operation is called "blooming."

In woollen printing the cloth is sometimes prepared with stannate of soda in a similar manner to that mentioned for calico. The woollen cloth is padded twice in stannate of soda (16° Tw.), and then passed through dilute sulphuric acid. The usual treatment with chloride of lime follows.

Application to Silk.—*Stannous Chloride* is employed in conjunction with catechu to produce heavily weighted blacks on a bottom of ferric oxide or Prussian blue (see *Catechu* and *Logwood*).

Stannic Chloride in form of tin spirits has been used in the dyeing with the natural colouring matters; but such application has become rare since the introduction of the artificial dyestuffs.

Stannic chloride is sometimes used for the weighting of white or light-coloured silk. The silk is generally used in the raw state, since it would have to be soaped again after being mordanted. The material is steeped in a solution of stannic chloride (32° to 48° Tw.) until it has become thoroughly impregnated with the solution. (The liquor is kept in a stone vat.) The fixation of the tin may be effected by merely dissociating the stannic chloride with water. For this purpose the well-saturated silk is wrung out, and the excess of liquor returned to the bath; the silk is then rinsed in running water to precipitate stannic hydroxide in the fibre, while a soluble acid salt is removed by washing. Frequently a cold diluted solution of soda is used for the fixation. The weight of the silk can be increased up to 25 per cent. by repeated operations. The solution of stannic chloride must not be too strong, since the silk shrinks perceptibly in a solution of the salt at 50° Tw., and begins to dissolve in a liquor at 100° Tw.

Repeated soapings at the boil are necessary to restore the natural feel to the silk, and it is always prone to deteriorate after some time under the influence of light. The tin has also an injurious effect on some of

the colours which are afterwards applied. If these colours are not dulled too much by such treatment the silk is often weighted first with stannic chloride and, subsequently, with tannin (tannic acid, sumach, or catechu).

It may also be mentioned that the strong solutions of stannic chloride which are used for weighting are difficult to work with on account of their strong corrosive action on the hands of the workmen.

The tin which is contained in the wash waters or soap-baths can be recovered by precipitation with lime, chalk, soda, tannin, or other substances. The precipitate is filtered off and either reconverted directly into stannic chloride, or, better, reduced to the metallic state by well-known metallurgical processes. The process which seems also to be applicable to waste tin liquors from black silk dyeing is now in general use in Lyons, and has been patented by the Lyons house Bonnet, Ramel, Savigny, Girandet et Marnas.*

Stannate of soda is not used in silk-dyeing.

COPPER (*Cuprum*), Cu = 63.4.

Copper is bivalent. It is a red-coloured metal of 8.94 specific gravity, which melts at a bright red heat and is slightly volatilised by white heat; it is very malleable and ductile and the best conductor of heat and electricity. Copper does not oxidise either in dry or in moist air at the ordinary temperature; but when strongly heated it is first covered with a thin film of oxide, reflecting the colours of the spectrum, and is slowly converted into scales of oxide of copper. Under the influence of the carbonic acid in the atmosphere it is converted into basic carbonate of copper. Steam is not decomposed by red-hot copper. Hydrochloric acid dissolves this metal only when in a very fine state of division, with evolution of hydrogen. Nitric acid, both concentrated and diluted, dissolves copper, even in the cold, but more rapidly when heated, forming nitrate of copper with evolution of nitrous gases. Sulphuric acid does not act on copper at the ordinary temperature; when heated with the strong acid the metal is dissolved and copper sulphate formed, while sulphur dioxide escapes.

Many valuable alloys contain copper as their chief constituent—*e.g.*, brass and all kinds of bronze.

Copper combines in four proportions with oxygen, of which only the two following possess more than a scientific interest:—

Cuprous Oxide, Cu_2O (Red Oxide).

Cupric Oxide, CuO (Black Oxide).

Cuprous Oxide, Cu_2O , is formed by heating a solution of copper sulphate with sugar and copper sulphate. It is a bright red powder

* *Journ. Soc. Dyers and Col.*, 1889, p. 159.

that does not oxidise in the dry state. It is used in glass painting, and imparts to the glass a fine ruby-red colour.

A yellow *hydroxide* of the composition $4\text{Cu}_2\text{O} + \text{H}_2\text{O} = \text{Cu}_8\text{O}_3(\text{OH})_2$ is obtained by precipitating cuprous chloride with caustic soda. This compound oxidises readily in the air. Cuprous oxide and hydroxide are readily soluble in ammonia; the colourless solution rapidly becomes blue by oxidation when exposed to the air.

Cupric Oxide, Cu O (*Black Oxide* or *Monoxide of Copper*).—Cupric oxide is a black amorphous, slightly hygroscopic powder which is insoluble in water, but dissolves readily in acids. Copper oxide dissolves readily in ammonia with a beautiful intensely blue colour; the ammonio-cupric liquid has the power of dissolving cellulose (cotton and other vegetable fibres); the presence of considerable quantities of mineral salts prevents the cellulose from dissolving in the liquid or precipitates it from the solution. Cupric oxide gives off its oxygen readily in presence of reducing substances, and acts as an oxidising agent.

Cupric Hydroxide, $\text{Cu}(\text{OH})_2$, is obtained as a light blue precipitate on addition of caustic alkalies to the solution of a cupric salt. It can be dried over lime without changing; the freshly precipitated moist hydroxide when dried at 100° becomes black and loses water, a hydroxide ($\text{Cu}_3\text{O}_2(\text{OH})_2$) being formed. Cupric hydroxide does not dissolve in alkalies and has no acid character; it is a moderately strong binacid base.

Cuprous Salts are little known in the pure state, since most acids decompose them, separating the metal in the free state, and forming cupric salts. The salts are colourless, and rapidly absorb oxygen from the air, forming cupric salts.

Cuprous Chloride, Cu_2Cl_2 , is obtained as a solid white substance by dissolving a mixture of metallic copper and cupric oxide in hydrochloric acid.

Cuprous Sulphocyanide or **Thiocyanate**, $\text{Cu}_2(\text{CNS})_2$, is used by calico-printers under the name *White Paste*. It is obtained by precipitating a solution of blue vitriol, containing ferrous sulphate or sulphurous acid with potassium sulphocyanide. The white precipitate is insoluble in water. It is used for the production of aniline black.

Cupric Salts.—Most of the normal salts are soluble in water. The soluble salts redden blue litmus, and have a disagreeable taste; they are decomposed at a low red heat, except blue vitriol, which withstands a slightly higher temperature. The salts are white in the anhydrous state; when they contain water they have a blue or green colour, which is perceptible in very diluted solutions. All compounds of copper are poisonous.

Caustic potash and soda precipitate from the solutions cupric hydroxide; alkaline carbonates precipitate insoluble basic cupric car-

bonate; ammonia in excess produces an intensely blue solution of a basic double salt; the carbonate of ammonia acts in the same manner. Sulphuretted hydrogen and ammonium sulphide precipitate from the solutions of copper salts black *copper sulphide* (Cu S), which is insoluble in diluted acids and in alkalies and little soluble in alkaline sulphides. Metallic iron in contact with solutions of copper salts is immediately coated with a film of copper, and is rapidly dissolved; the copper in the salt is replaced by iron—



Basic Salts of Copper are insoluble in water.

Cupric Sulphate, $\text{Cu S O}_4 + 5 \text{ H}_2 \text{ O}$ —*Blue Vitriol, Blue Stone, Copper Sulphate*.—Cupric sulphate is manufactured by roasting ores which contain copper and by dissolving them in sulphuric acid. From this solution crystals having different degrees of purity are obtained; the chief impurity is iron. Cupric sulphate crystallises in transparent, blue triclinic crystals, which contain only 5 molecules of water of crystallisation, whereas the other metallic sulphates, known as “vitriols,” *e.g.*, ferrous sulphate, contain 7 molecules. 100 parts of water dissolve at—

10° C.	20° C.	30° C.	50° C.	70° C.	90° C.	100° C.
Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
37	42	49	66	95	156	203

Blue vitriol is insoluble in absolute alcohol, and but slightly soluble in diluted alcohol. It loses 4 molecules of water at 100° and the last at 220° to 240°, forming a white mass. The anhydrous salt attracts water with great avidity, and turns blue; use is made of this reaction to demonstrate the presence of water in organic liquids, *e.g.*, alcohol. Blue vitriol is extensively used in the arts; for example, in the manufacture of copper colours, in dyeing and calico-printing.

Cupric Chloride, Cu Cl_2 , is formed when copper is acted upon by chlorine gas, or when cupric oxide or carbonate is dissolved in hydrochloric acid. It forms a brownish-yellow powder in the anhydrous state, and crystallises in bluish-green rhombic crystals ($\text{Cu Cl}_2 + 2 \text{ H}_2 \text{ O}$). Cupric chloride is very soluble in water and in alcohol, and is deliquescent. The alcoholic solution burns with a beautiful green flame.

Cupric Nitrate, $\text{Cu (N O}_3)_2$, is obtained by dissolving copper or cupric oxide in nitric acid. Calico-printers prepare it also by the double decomposition of blue vitriol and lead nitrate. The salt forms fine blue prisms, $\text{Cu (N O}_3)_2 + 3 \text{ H}_2 \text{ O}$. On being heated to 65° nitric acid is given off; hence the anhydrous salt is not known. Cupric nitrate is very soluble in water and is deliquescent. Since it is

decomposed at comparatively low temperatures it is a strong oxidising agent.

Cupric Carbonate, Cu C O_3 , is not known in the pure state. By adding a solution of an alkaline carbonate to a cupric salt, a basic salt, $\text{Cu C O}_3 + \text{Cu (O H)}_2$, is obtained which is insoluble in water. Various minerals consist of basic cupric carbonates.

Cupric Acetate, $\text{Cu (C}_2\text{H}_3\text{O}_2)_2 + \text{H}_2\text{O}$, is obtained by dissolving cupric oxide, verdigris, or a carbonate of copper in acetic acid, or by the double decomposition of copper vitriol and lead acetate. It forms dark bluish-green monoclinic crystals, which effloresce in the air and dissolve in 13.4 parts of cold and in 5 parts of hot water, also in alcohol. The solution gives off acetic acid on boiling. An *acid salt*, $\text{Cu (C}_2\text{H}_3\text{O}_2)_2 \text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O}$, has been prepared.

Basic cupric acetate or *blue verdigris* is $2 \text{Cu (C}_2\text{H}_3\text{O}_2) (\text{O H}) + 5 \text{H}_2\text{O}$. It is prepared by placing sheets of copper into acetic acid or into the fermenting husks of grapes. The salt forms blue crystals, and occurs in commerce in greenish-blue lumps, which also contain basic cupric carbonate and sometimes gypsum. On treatment with water the salt is decomposed into the normal and a more basic salt: *green verdigris*, $2 \text{Cu (C}_2\text{H}_3\text{O}_2)_2, \text{Cu O}$. Still more basic cupric acetates are also known.

Copper Sulphide, Cu S , is obtained as a black precipitate by passing a current of sulphuretted hydrogen through a solution of a copper salt. Lauber (*Zeugdruck*, II., p. 43) gives the following instructions for preparing copper sulphide: mix 1250 grms. ($1\frac{1}{4}$ lb.) of flowers of sulphur with 5 litres ($\frac{1}{2}$ gall.) caustic soda (70°Tw.), and heat on the water bath, with frequent stirring, until all is dissolved (3 to 4 hours); pour the solution, with constant stirring, into a solution of 6 kgs. (6 lbs.) of blue vitriol in 150 litres (15 galls.) of tepid water, allow the precipitate to settle, and wash it several times with tepid water, by decanting; to the filtered paste of copper sulphide, which should amount to 12 kgs. (12 lbs.), add 15 grms. ($\frac{1}{4}$ oz.) of ammonium sulphide, in $\frac{1}{2}$ litre (1 pint) of water to protect the copper sulphide against the oxidising action of the air and store it in vessels in which it is protected from the air. Copper sulphide is insoluble in water, in diluted acids, and in alkalies; by oxidation it is readily converted into cupric sulphate. It is used in the printing and dyeing of aniline-black.

APPLICATION OF THE SALTS OF COPPER TO THE TEXTILE FIBRES.

The salts of copper are chiefly used in dyeing as oxidising agents. They act as carriers of oxygen, which they readily give up to oxidisable substances, and take up again from the air or from bodies which are easily deoxidised.

Application to the Vegetable Fibres.—Copper salts are employed in cotton-dyeing and cotton-printing as oxidising agents, in the way above mentioned, for the production of cutch-browns and logwood-blacks; they serve, however, to a certain extent as actual mordants. Copper sulphate is frequently employed in the black-dyeing of cotton warp in union goods, and is fixed for this purpose by means of tannin. Copper sulphide is used in the production of aniline-black by printing, while copper sulphate is largely used in the dyeing of aniline blacks on piece goods. Recently a process has been patented for rendering certain colours, *e.g.*, benzoazurin, faster to light, by treatment with salts of copper. This reaction has been explained by M. Scheurer* by the suggestion that the colour is coated by a thin film of a copper compound which absorbs the active rays of light.

Application to Wool.—Copper sulphate is used in conjunction with aluminium sulphate and with ferrous sulphate in the dyeing of logwood-blues and logwood-black. It is also frequently employed along with bichromate of potash in the mordanting of wool. Generally the natural mordant-dyestuffs resist the bleaching action of the light best when dyed on copper mordants. Very often copper sulphate is used as a saddening agent after the wool has been boiled in a decoction of the colouring matter.

Application to Silk.—Copper sulphate and acetate are used in saddening certain shades of logwood-black on silk.

LEAD (*Plumbum*), Pb = 207.

Lead is bivalent or tetravalent. It is a bluish-white, bright and very soft metal of 11.3 specific gravity; it melts at 324° C. and boils at a white heat; it possesses little tenacity and elasticity. The bright surface of the metal becomes tarnished in moist air by the formation of a film of oxide. Lead when melted in open vessels is oxidised, and on the surface forms a mixture of lead and lead oxide, so-called lead ashes. Lead is a very useful metal, which could hardly be replaced in many industries, since it is very slowly acted upon by acids, especially at the ordinary temperatures. Acetic acid makes an exception to this rule, so does hydrochloric acid.

Lead is a constituent of many important alloys, such as solder, pewter, &c.

Lead forms the following five oxides:—

Lead Suboxide, Pb_2O .

Lead Monoxide or Litharge, PbO .

Lead Sesquioxide, Pb_2O_3 .

Red Lead or Red Oxide of Lead, Pb_3O_4 .

Lead Dioxide or Peroxide, PbO_2 .

* *Journ. Soc. Dyers and Col.*, 1891, p. 26.

The suboxide and sesquioxide are of no practical importance.

Lead Monoxide, Pb O , is obtained by melting lead with access of air. It forms a straw-coloured powder, called *Massicot*; or, when fused at red heat, lemon-yellow to orange-coloured scaly crystals, called *Litharge*. It has a specific gravity of 9.36, is not soluble in water, but imparts to the latter an alkaline reaction by generating the hydroxide. It dissolves in hot solutions of caustic potash or soda, as also in nitric and acetic acid; in most of the other mineral acids it is insoluble. It has basic properties; for example, it saponifies fats, forming lead salts of the fatty acids (lead plasters).

Lead Hydroxide, Pb (O H)_2 , is precipitated from the solutions of lead salts by caustic alkalies as a white voluminous mass; it is soluble in an excess of caustic potash or soda, forming *plumbates*; but is not soluble in ammonia. Lead hydroxide has a very feeble acid character; but it is a fairly strong diacid base.

Red Lead, $\text{Pb}_3 \text{O}_4$, is obtained by heating massicot in the air; it is a heavy fiery-red powder, insoluble in water. It is used as a pigment in glass making, and as a paint to prevent iron from rusting, and as a precipant for water- and steam-joints.

Lead Dioxide or Peroxide, Pb O_2 , also called *puce-coloured oxide of lead*, is obtained by treating red lead with nitric acid. It forms a brown powder which is insoluble in water. It is not readily attacked by acids, and does not form salts with them. Lead peroxide dissolves in hot solutions of caustic potash or soda forming alkaline *plumbates* ($\text{Na}_2 \text{ Pb O}_3$ and $\text{K}_2 \text{ Pb O}_3$). Lead peroxide and the plumbates are strong oxidising agents.

Lead Salts are generally colourless; those which are soluble in water redden blue litmus and have a disagreeable sweet metallic taste. All lead salts are very poisonous. Caustic alkalies precipitate from the solutions the hydroxide which redissolves in an excess of caustic potash or soda, but not of ammonia. Soda precipitates basic carbonate of lead. Hydrochloric acid and chlorides form a precipitate of lead chloride, which is soluble in much water. Sulphuric acid and sulphates precipitate insoluble sulphate of lead. Chromates precipitate chromate of lead (chrome-yellow), which is readily soluble in caustic potash or soda.

Sulphuretted hydrogen or sulphide of ammonium forms a precipitate of black lead sulphide, which is insoluble in alkaline sulphides, acids and alkalies; by hot nitric acid it is slowly decomposed. Lead salts, notably *white lead*, blacken in an atmosphere containing even traces of sulphuretted hydrogen, lead sulphide being formed.

Lead Nitrate, $\text{Pb (N O}_3)_2$, is prepared by dissolving the requisite amount of litharge in hot dilute nitric acid. A solution of the *basic nitrate of lead*, $\text{Pb (N O}_3)(\text{O H})$, is obtained by boiling a solution of the normal salt with the calculated amount of litharge.

Lead nitrate crystallises in regular crystals; it is sold in the form

of irregular lumps and frequently contains copper as an impurity. In alcohol it is almost insoluble. 100 parts of water dissolve at

0° C.	10° C.	25° C.	45° C.	65° C.	85° C.	100° C.
Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
39	48	60	80	101	120	139

Lead Acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$ —White Sugar of Lead.—Lead acetate is prepared by dissolving the calculated amount of litharge in hot acetic acid. The pure product, which contains over 99 per cent. of crystallised salt ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$), is called white sugar of lead. With crude acetic acid (pyroligneous acid) *brown sugar of lead* is prepared, which contains less than 90 per cent. of the pure salt. By using an excess of litharge, *basic acetate of lead*, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)(\text{OH})$, and still more basic salts are obtained.

The normal salt forms monoclinic crystals, which effloresce in the air and melt at 75°.

Lead acetate dissolves in about two parts of water at the ordinary temperature and is readily soluble in diluted, not in absolute, alcohol. The solutions of lead acetates rapidly absorb carbon dioxide from the atmosphere and become turbid by formation of the carbonate.

White lead is a basic carbonate of lead.

APPLICATION OF THE LEAD SALTS TO THE TEXTILE FIBRES.

Acetate and nitrate of lead are frequently used in the preparation of mordants, since they readily exchange their acid for sulphuric acid by double decomposition, sulphate of lead being insoluble. Except for the production of chrome-yellows the lead salts are little used in dyeing. The colours are liable to be blackened by sulphuretted hydrogen and are not brilliant. They are poisonous.

Cotton seems to possess some affinity for lead, since it retains the same with great tenacity. Chrome-yellow and chrome-orange are produced extensively on cotton by impregnating the fibre with a lead salt and passing through bichromate. In this case the lead salt may be considered to act as a real mordant. In conjunction with fatty acids lead salts serve also as mordants for the eosins.

Silk is sometimes weighted with basic acetate of lead.

MANGANESE, Mn. = 55.

Manganese is a metal which is either di-, tetra-, hexa-, or hepta-valent, and forms the following six oxides:—

Manganese Monoxide or Manganous Oxide, Mn O .

Red Manganese Oxide or Mangano-Manganous Oxide, $\text{Mn}_3 \text{O}_4$.

Manganese Sesquioxide or Manganic Oxide, $\text{Mn}_2 \text{O}_3$.

Manganese Dioxide or Black Oxide of Manganese, Mn O_2 .

Manganic Anhydride (not known in the free state), Mn O_3 .

Manganese Heptoxide, $\text{Mn}_2 \text{O}_7$.

Manganese Monoxide, Mn O , is a greenish powder which rapidly absorbs oxygen, forming red oxide ($\text{Mn}_3 \text{O}_4$).

Manganous Hydroxide, Mn (O H)_2 , is precipitated from the solutions of manganous salts as a white gelatinous mass that rapidly turns brown by absorption of oxygen. It is soluble in most acids and is a binacid base; the salts are colourless or pink and do not absorb oxygen. Manganous hydroxide is insoluble in caustic alkalies. Sulphide of ammonium precipitates manganous sulphide from the solutions of manganous salts; sulphuretted hydrogen has little action except in the presence of free alkali.

Manganic Oxide, $\text{Mn}_2 \text{O}_3$, is formed as a black powder when one of the other oxides is heated in oxygen gas.

Manganic Hydroxide, $\text{Mn}_2 (\text{O H})_6$, is a dark brown precipitate obtained by the oxidation of manganous hydroxide. It is a weak hexacid base, insoluble in alkalies and not readily soluble in acids. It does not form well-defined salts.

Manganese Dioxide, Mn O_2 , peroxide of manganese, the common black ore of manganese or pyrolusite, is a dark grey, almost black, crystalline mass.

Manganese dioxide forms hydroxides, which act as very weak bases and acids; the salts which it forms with acids are called manganic salts; those in which it combines with bases are the manganites. Manganese dioxide dissolves in cold hydrochloric acid without evolution of chlorine; but on heating it, the Mn Cl_4 dissociates into manganous chloride and chlorine:—



The use of manganese dioxide in the manufacture of chlorine gas, chloride of lime, and chlorates, is based on this reaction.

Manganic Acid, $\text{H}_2 \text{Mn O}_4$, is not known in the free state, neither is the anhydride (Mn O_3). *Potassium Manganate*, $\text{K}_2 \text{Mn O}_4$, is obtained as a bright green mass when an oxide of manganese is fused in the air with caustic potash. The aqueous solution yields this salt in a crystalline form; on standing, however, or when acidified, the green colour of the solution is changed into bright purple and a new salt is formed: *Potassium Permanganate*, K Mn O_4 (see below), whilst hydrated manganese dioxide is deposited:—



Inversely potassium permanganate is reduced to potassium manganate

by boiling it with a concentrated solution of caustic soda and by the action of reducing agents.

Manganese Heptoxide, Mn_2O_7 , and the hydrate, *Permanganic Acid*, H Mn O_4 , are unstable and little known compounds.

Manganous Chloride, Mn Cl_2 , is obtained as a bye-product in the manufacture of chlorine from hydrochloric acid by means of manganese dioxide (see above). It forms monoclinic pink-coloured deliquescent crystals, which contain four molecules of water of crystallisation. It is soluble in water and in alcohol; the alcoholic solution when ignited burns with a red flame. 100 parts of water dissolve at 10° , 150 parts; at 31° , 269 parts; and at $62^\circ\cdot5$, 625 parts of the salt, $\text{Mn Cl}_2 + 4 \text{ H}_2\text{O}$.

Manganous chloride is used in dyeing cotton manganese-brown or -bronze. The cotton is impregnated with a solution of the salt, passed through caustic alkali, and the precipitated hydroxide is oxidised by the air or other oxidising agents to form brown manganic hydroxide. The oxidising power of manganic hydroxide which has been thus deposited in the fibre may be used for the production of aniline-black. The product comes into commerce as a reddish solution at about 70°Tw . It often contains calcium chloride as an impurity.

Potassium Permanganate, K Mn O_4 —*Permanganate of Potash*.—Potassium permanganate is found in commerce in the form of almost black crystals with a steel-blue lustre; it dissolves with an intense crimson colour in 15 to 16 parts of cold water.

Potassium permanganate is a very powerful oxidising agent in acid, in alkaline, and in neutral solutions. Hence, it is largely used in the laboratory and as a disinfectant (Condy's fluid), and it is sometimes employed to destroy colours on the fibres which cannot be removed in any other way. Some dyers use it to produce manganese-bronze, and it has recently been suggested as a substitute for chlorine in the "preparing" of wool for printing.

ANTIMONY (*Stibium*), $\text{Sb} = 120$.

Antimony is tri- and pentavalent. It resembles phosphorus and arsenic in some respects; but it bears still greater resemblance to the metals. It is considered by some as a metal, by others as a metalloid. Antimony forms a bluish-white crystalline, brittle mass of 6·8 sp. gr. It is a constituent of many important alloys—*e.g.*, type metal, Britannia metal, and anti-friction metal. Compounds of antimony are used in pharmacy and in dyeing.

Antimony forms the following compounds with oxygen:—

Antimony Trioxide, Sb_2O_3 ; Antimonious Acid, H Sb O_2 .

Antimony Tetroxide, Sb_2O_4 ; Hypoantimonious Acid, $\text{H}_2\text{Sb}_2\text{O}_5$.

Antimony Pentoxide, Sb_2O_5 ; $\left\{ \begin{array}{l} \text{Antimonic Acid, H Sb O}_3 \\ \text{Metantimonic Acid, H}_2\text{Sb}_2\text{O}_7 \end{array} \right.$

Antimony Trioxide, Sb_2O_3 , is found in nature, and can be prepared by heating antimony in the air or with diluted nitric acid. It forms white crystals, which melt at a red heat; it is very sparingly soluble in water, not soluble in nitric acid, but dissolves in hydrochloric, sulphuric, or tartaric acid, and in caustic alkalies.

Antimony trioxide forms a hydroxide, *antimonious acid*, H Sb O_2 . This compound acts both as an acid and as a base. The acid character does not offer any practical interest. As a base it is both monovalent and trivalent; in the monovalent state it is considered to be combined with oxygen, forming the monovalent radical *antimonyl*, Sb O . The salts which antimony forms with acids, when soluble in water, redden blue litmus, and possess a very disagreeable metallic taste. They are dissociated by water, antimony trioxide being thrown down, and an acid salt remaining in solution. Caustic alkalies and the alkaline carbonates precipitate from the solutions of antimony salts antimonious hydroxide (H Sb O_2), which is converted into antimony trioxide on boiling. The hydroxide is soluble in an excess of caustic potash and soda. Sulphuretted hydrogen precipitates from acidified solutions of the salts orange-red antimonious sulphide (Sb_2S_3), which is soluble in alkaline sulphides.

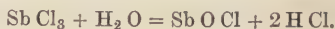
Antimony and its compounds are poisonous. Since it shows reactions similar to arsenic, it is sometimes mistaken for the latter; the poisonous effects of antimony and arsenic, however, are totally different.

The application of compounds of antimony in dyeing is limited to the salts of antimony trioxide, and these are employed exclusively in dyeing and printing of cotton and linen. Their usefulness is based on the fact that tannic acid forms a lake with antimony trioxide, which is insoluble in tannic acid. Faster colours are obtained with antimony tannate than with tannic acid alone (see pp. 180 and 181).

Antimonious Sulphate, $\text{Sb}_2(\text{S O}_4)_3$, separates from the solutions of antimony trioxide in hot conc. sulphuric acid on cooling. It is dissociated by water into an insoluble basic and a soluble acid salt.

Antimonyl Sulphate, $(\text{Sb O})_2\text{S O}_4$, is obtained by dissolving antimony trioxide in moderately diluted sulphuric acid. It is dissociated by water, like the preceding compound.

Antimony Chloride or **Trichloride**, Sb Cl_3 , is formed by the action of chlorine on antimony. It is prepared by dissolving antimony trioxide or sulphide in hydrochloric acid, and can be evaporated to dryness from this solution. It forms a soft, crystalline, colourless mass, which melts at 73° , and volatilises at 223° ; it is deliquescent, and is dissociated by much water, according to the equation—



Antimony Fluoride, Sb Fl_3 , is obtained by dissolving antimony trioxide in hydrofluoric acid. The salt forms colourless rhombic

pyramids, which are deliquescent; by dilution with water it is not decomposed; on evaporating the solution without excess of hydrofluoric acid a basic fluoride is obtained. Antimony fluoride attacks glass and metals, except lead and platinum. It is kept in wooden casks.

Antimony fluoride forms crystalline double salts with one, two, or three equivalents of the fluorides, chlorides, and sulphates of the alkalies.

Antimony Sodium Fluoride, $\text{Sb F}_3 \text{ Na F}$, has been brought into the market by R. Koepp & Co., in Oestrich a. Rh. (Germany), under the name of *double antimony fluoride*. It crystallises in triclinic prisms, and is readily soluble in water; 100 parts of cold water dissolve 63 parts of the salt, and 100 parts of hot water 166 parts. The solution can be diluted without dissociation. It reacts slightly acid, and corrodes glass and metals.

The salt contains 66 per cent. $\text{Sb}_2 \text{ O}_3$ (*i.e.*, the corresponding amount of Sb F_3), and 658 grms. are equivalent to 1,000 grms. of tartar emetic.

A double salt of antimony fluoride and ammonium sulphate, $\text{Sb F}_3 (\text{N H}_4)_2 \text{ S O}_4$, has been patented, and is sold by E. de Haën, List vor Hannover (Germany), under the name of *antimony salt*. It forms white oblique crystals, and dissolves very easily in water—140 parts of the salt in 100 parts of water; the solution possesses a strongly acid reaction, and attacks glass and metals like the other fluorides. It is not dissociated by dilution. The salt contains an amount of antimony fluoride corresponding to 47 per cent. $\text{Sb}_2 \text{ O}_3$ —*i.e.*, 9 parts of antimony salts are nearly equivalent to 10 parts of tartar emetic. A number of similar salts are sold by various firms as substitutes for tartar emetic.

Double Oxalate of Antimony and Potassium, $\text{Sb K}_3 (\text{C}_2 \text{ O}_4)_{\frac{3}{2}} + 4 \text{ H}_2 \text{ O}$, has been introduced to the dyeing trade by R. Koepp & Co. in Oestrich. The salt is obtained by dissolving antimony trioxide in acid oxalate of potash, and crystallises in fine needles, which are stable in the air, and dissolve most readily in either cold or hot water. The solution of the salt dissociates rapidly, forming an insoluble basic oxalate of antimony and soluble acid oxalates. The double oxalate contains only 25.1 per cent. $\text{Sb}_2 \text{ O}_3$; it has been found, however, that it can replace equal quantities of tartar emetic, although the latter contains 43.4 per cent. $\text{Sb}_2 \text{ O}_3$. Noelting has explained this surprising fact by experiments, showing that acid potassium oxalate does not prevent the formation of antimony tannate to the same extent as acid potassium tartrate, which is generated from tartar emetic. On the other hand the double oxalate dissociates more rapidly than the double tartrate, thus yielding its antimony more readily, and for these two reasons it is more effective.

Double Tartrate of Antimony and Potassium or Tartar Emetic, $(\text{Sb O}) \text{ K C}_4 \text{ H}_4 \text{ O}_6 + \frac{1}{2} \text{ H O}_2$, was introduced into the dyeing

trade about ten years ago by Thomas Brooks of Manchester, who was the first to use an antimony salt for the fixation of basic colours by means of tannic acid, and was rewarded for his invention by the Société Industrielle de Mulhouse with a gold medal.

Tartar emetic is obtained by boiling antimony oxide with a solution of tartar, and crystallises with half a molecule of water in rhombic octahedra which lose water by efflorescence. The salt is not very soluble in water, and insoluble in alcohol. One part of tartar emetic, $(\text{Sb O}) \text{K C}_4\text{H}_4\text{O}_6 + \frac{1}{2} \text{H}_2\text{O}$, requires for its solution at—

87° C.	21° C.	31° C.	50° C.	75° C.
Parts Water.	Parts Water.	Parts Water.	Parts Water.	Parts Water.
19	12.6	8.2	5.5	3.2

The solution dissociates into insoluble basic antimony tartrate and soluble acid tartrates. Pure antimony-potassium tartrate $(\text{Sb O}) \text{K C}_4\text{H}_4\text{O}_6 + \frac{1}{2} \text{H}_2\text{O}$ contains 43.4 per cent. Sb_2O_3 .

The commercial product is sold at a strength of 43 per cent. Sb_2O_3 in fine crystals or irregular lumps. The article is subject, however, to adulteration either with cheaper antimony salts or with other substances; it may contain the required quantity of antimony without being genuine tartar emetic.

Antimony Lactate has been patented* for the same applications in dyeing and printing for which the other antimony salts are used. The salt is said to be not crystallisable, very soluble in water, and not to dissociate. It does not appear to be offered to the trade.

APPLICATION OF THE COMPOUNDS OF ANTIMONY TO THE TEXTILE FIBRES.

Tannic acid is employed in the dyeing of cotton and linen as a mordant, because it forms lakes with the basic dyestuffs, which are insoluble in water. An excess of tannic acid, the presence of which is unavoidable, dissolves these lakes, hence the colours thus obtained do not resist washing and soaping, and are liable to bleed. It has been found, however, that tannic acid can be transformed by certain metals, for example, by tin, aluminium, iron, and zinc, but best of all by antimony, into insoluble salts, which have the same power as is possessed by the free acid to precipitate basic dyestuffs in the fibres, but have no dissolving action on the colour lakes. These double lakes have the additional advantage of resisting the bleaching action of light better than the simple tannates.

Thomas Brooks, as has been mentioned, discovered the use of

* Ch. N. Waite, U.S. Patent 341294.

antimony salts in the form of tartar emetic for the fixation of aniline colours. Tartar emetic, however, is a very expensive article, since the tartaric acid in it has a much higher value than the antimony. During the last few years a number of substitutes, notably the double oxalate and various fluorides, have been introduced, which are sold at considerably lower prices and give more or less satisfactory results. It seems that tartar emetic acts better than any of these substitutes and requires the least amount of care in application, especially in calico-printing; it can be replaced, however, in most cases by other salts of antimony.

The application of the antimony salts is very simple. The goods which have been mordanted with tannic acid are slightly rinsed in cold water to remove loosely adhering mordant and then worked for one-quarter of an hour in the tepid solution (30° to 60°) of the antimony salt. The bath can be used continuously, if the liberated acid is neutralised from time to time. The goods which have been worked in the antimony bath are wrung out and must be well washed in water before dyeing; a hot soaping improves the ultimate shade as to brilliancy and is advisable for some colours—*e.g.*, methylene-blue. The washing must be done with the greatest care, since loosely adhering antimony tannate, unless removed before dyeing, will be the cause of rubbing and smearing of the colour. Moreover, antimony is a strong poison, and such loosely adherent particles are liable to cause serious affections of the skin.

In printing, the application is different in so far as the goods are printed on with a mixture of tannic acid and dyestuff, steamed, and subsequently passed through the antimony bath. In printing, the lake formed by tannic acid and dyestuff is transformed into the triple antimony lake; whereas in dyeing, antimony tannate is formed first and combines subsequently with the dyestuff.

In the dyeing of cotton and linen goods a solution of 5 to 10 parts of tartar emetic in 1,000 parts of water is used; the tannic acid previously absorbed by the fibre extracts antimony from this solution, whilst an acid potassium tartrate is left behind, which impedes and prevents the formation of antimony tannate. This acid salt can be neutralised by the addition of sodium carbonate: but it is difficult to regulate properly the quantity of soda to be added; better results are obtained by adding to the solution a small quantity of ground chalk which dissolves more gradually.

Antimony potassium oxalate is used of the same strength as tartar emetic, although it contains only about half as much antimony; it is best to use 5 to 10 parts per 1,000 parts of water; greater quantities give less satisfactory results. The action of the oxalate is more rapid than that of the tartrate; it works best in diluted baths and by short immersion. Calcareous water should be avoided, since it precipitates oxalic acid; and the addition of soda does not appear to be advantageous.

The fluorides, as a rule, are very acid and must be neutralised with soda; about one-fifth to one-fourth of their weight of soda crystals is required. The usual strength employed is 5 to 20 parts of salt to 1,000 parts of water; it yields good results, but the shades are not exactly the same as those obtained with tartar emetic.

Kertecz has proposed the use of antimony trichloride precipitated by soda. The antimonious acid, although little soluble in water, is taken up in the precipitated state; the results obtained with this agent, however, are not very good; it appears to be necessary that the antimony should be absorbed in a soluble state and that it should be able to form a precipitate with the tannic acid in the interior of the fibre.

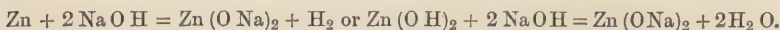
Zinc, $Zn = 65$.—Zinc is bivalent. It is a bluish-white metal of 6.9 sp. gr., exhibits crystalline structure, and is brittle at the ordinary temperature, but it can be rolled out at $130^{\circ}C$. It melts at 423° and volatilises at a bright red heat; it takes fire at this temperature and burns with a luminous green flame, forming zinc oxide (ZnO). Zinc is not acted upon by dry or moist air, nor is it affected by water; but it dissolves readily in dilute acids or in solutions of caustic potash or soda, with the evolution of hydrogen.

Zinc is much used in the metallic state in the form of sheets, and is employed as a coating for iron to protect the latter metal from rust; the iron which has thus been coated is, incorrectly, called galvanised iron. Zinc dust, which is formed in great quantities by the metallurgical distillation of zinc, consists of a mixture of finely-divided zinc and zinc oxide; it is an excellent reducing agent in acid and especially in alkaline solutions. It is used both in the laboratory and in the arts; for instance, for the preparation of indigo-vats.

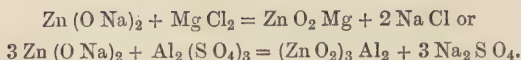
Zinc forms a number of industrially important alloys.

Zinc Oxide, ZnO , is a white substance which is obtained by the oxidation of zinc or by igniting the carbonate or nitrate. Zinc oxide forms the white pigment called *zinc white*; it has the advantage of not being discoloured by sulphuretted hydrogen.

Zinc Hydroxide, $Zn(OH)_2$, is precipitated as a white amorphous mass from the solutions of zinc salts by caustic potash, soda, or ammonia; by an excess of either precipitant it is readily redissolved. Neither zinc oxide nor zinc hydroxide are soluble in water, but freely soluble in caustic alkalies and dilute acids. Zinc hydroxide is a diacid base and a weak di-basic acid. The compounds with bases are called *zincates*; they are formed by dissolving zinc or zinc oxide or zinc hydroxide in caustic alkalies; for instance, according to the equations,—



The zincates of the alkalies are precipitated by the salts of the other metals, forming zincates with the latter, for instance—



By means of this reaction, compound mordants, consisting of two or three different metals, are precipitated in the fibre. The goods are first impregnated with acetate of aluminium or chromium, for instance, and subsequently passed through sodium zincate; a triple mordant, consisting of aluminium, magnesium, and zinc, is obtained by passing the material, first, through a mixture of the acetates of aluminium and magnesium, and, subsequently, through sodium zincate. (See *St. Denis red* and *Gallocyanin*.) An extensive study of the compound mordants has been published recently by Prudhomme* in the *Bulletin de Mulhouse*, 1891.

The *zinc salts* are colourless and soluble in water or in acids. The neutral salts, which are soluble in water, redden litmus, possess a disagreeable metallic and astringent taste, and are poisonous.

Zinc Sulphate or *White Vitriol*, $\text{Zn S O}_4 + 7 \text{ H}_2 \text{O}$, crystallises in long prisms, and is isomorphous with Epsom salt (magnesium sulphate). It is efflorescent in the air and loses six molecules water at 100° ; it is decomposed by white heat.

The anhydrous salt, Zn S O_4 , dissolves in twice its weight of cold water, and 100 parts of cold water dissolve about 135 parts, and 100 parts of hot water 655 parts of the crystallised salt. Zinc sulphate is used for weighting cotton goods and sometimes in dyeing wool with the basic colours.

Zinc Chloride, Zn Cl_2 , is a white, soluble, deliquescent substance. The aqueous solution gives off hydrochloric acid on boiling and a basic salt, *zinc oxychloride*, Zn Cl (O H) , is formed, which can also be obtained by boiling zinc chloride with oxide or hydroxide of zinc. By adding water to the solution of the basic salts, precipitates of varying composition are obtained, consisting of the zinc oxychloride and of zinc hydroxide. By boiling a solution of zinc chloride (1.70 sp. gr.) with an excess of zinc oxide a solution is obtained, which dissolves silk. This solution is used in the analysis of mixed fabrics to separate silk from wool and from the vegetable fibres.

Zinc chloride extracts the elements of water from organic compounds. Hence it is used as a caustic in surgery and as a preservative in the arts, while it is frequently employed in the laboratory. It is largely used as a constituent of the size for cotton goods. Its action is simultaneously hygroscopic and antiseptic.

Zinc Nitrate, $\text{Zn (N O}_3)_2 + 6 \text{ H}_2 \text{O}$, is a crystalline deliquescent salt. On being heated to 100° it loses water and nitric acid and a basic salt is formed.

Zinc nitrate is used by printers, and is prepared either by dissolving zinc in nitric acid or by the double decomposition of zinc sulphate and

* *Journ. Soc. Dyers and Col.*, 1891, p. 133.

lead nitrate; iron can be removed from the solution of this salt by boiling it with zinc oxide. Zinc nitrate is added to the thickened mordants, since it prevents the thickening from prematurely decomposing. On account of its hygroscopicity it is also sometimes added to colours in woollen printing.

Zinc Carbonate, Zn CO_3 , occurs native as calamine. It is obtained by precipitating a zinc salt with acid potassium carbonate; if the solution of normal potassium carbonate is added, basic carbonates of zinc of varying composition are thrown down.

Zinc Acetate, $\text{Zn (C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$, forms crystals which are readily soluble in water.

This salt has been recommended by Henry Schmid for the fixation of tannic acid instead of tartar emetic; 8 to 10 parts of zinc sulphate and 4 to 5 parts of sodium acetate are added to 1000 parts of water. (See *Basic Colours*.)

Nickel, $\text{Ni} = 59$ (?).—Nickel is a bi- and tetravalent metal, which resembles iron chemically. It is a white, malleable and tenacious, very hard and magnetic metal of the sp. gr. 8.9. It is used in the free state for nickel-plating iron and other metals to protect them from oxygen and acids; it is also a constituent of various alloys, such as German silver and certain coins.

Nickel forms two oxides, the *monoxide* (Ni O) and the *sesquioxide* (Ni_2O_3); the former of these gives rise to nickel hydroxide and to the ordinary nickel salts.

Nickel Hydroxide, Ni (OH)_2 , is obtained as an apple-green precipitate on addition of caustic potash or soda to the solution of a nickel salt; an excess of the precipitant does not redissolve the hydroxide. It is slightly soluble in water and dissolves in ammonia with a blue colour. It is stable in the air and dissolves readily in sulphuric, nitric, or hydrochloric acid to form nickel salts.

Nickel Sesquioxide, Ni_2O_3 , is a black powder which dissolves in hydrochloric acid with the evolution of chlorine and formation of the same chloride as is obtained from the preceding nickel oxide.

The *nickel salts* are derived from nickel monoxide, and are prepared by the action of acids on the oxides or on the carbonate. They possess a peculiar apple-green colour; many of them are soluble in water. The most important soluble nickel salts are *nickel sulphate*, $\text{Ni SO}_4 + 7\text{H}_2\text{O}$, *nickel chloride*, Ni Cl_2 , *nickel-ammonium chloride*, $\text{Ni Cl}_2 \cdot \text{NH}_4\text{Cl}$, *nickel nitrate*, $\text{Ni (NO}_3)_2$, *nickel acetate*, $\text{Ni (C}_2\text{H}_3\text{O}_2)_2$, *nickel nitrate-acetate*, $\text{Ni NO}_3 (\text{C}_2\text{H}_3\text{O}_2)$, and *nickel sulphocyanide*, Ni (CNS)_2 .

Liechti and Ulrich* have studied the mordanting properties of various nickel salts on cotton. They succeeded in fixing them either by first impregnating the material with a nickel salt and subsequently passing it through soda; or by first mordanting with Turkey-red oil

* *Journ. Soc. Dyers and Col.*, 1887, pp. 81, 93.

and subsequently with a nickel salt. Many of the nickel salts crystallise in the fibre and lose their acid very slowly; hence they are little suitable for mordanting; the best results were obtained with the chloride, the nickel-ammonium chloride, the nitrate, the nitrate-acetate and sulphocyanide; while the sulphate and acetate are less serviceable owing to their great tendency to crystallise. These authors recommend the nickel-ammonium chloride for dyeing and the nickel nitrate-acetate for printing to produce pure colours in light shades.

The only use made of the nickel salts in dyeing or printing is for the fixation of the nitroso-colours, such as dinitrosoresorcin, &c.

W. M. Gardner* has recently studied the behaviour of nickel sulphate and cobalt sulphate as wool mordants. He found that these salts are fixed best without any oxalic acid, tartar, or other acid being added to the mordanting-bath. The salts apparently do not offer advantages over the iron salts, which they resemble in their tinctorial character.

Cobalt, Co = 59 (?).—Cobalt and its compounds resemble nickel and its salts. The cobalt compounds are distinguished for the brilliancy of their colour; some are employed as pigments, and they impart a magnificent blue tint to glass. There are three oxides of cobalt. The monoxide (Co O) forms with acids the stable *cobaltous salts*, which are pink coloured; such as the sulphate (Co S O₄ + 7 H₂O) or chloride (Co Cl₂). The tinctorial properties of the cobalt compounds have been little studied (see *Nickel*).

Various rare metals have been recommended as mordants, and some find a certain application in dyeing or printing. The most important of these is vanadium.

Vanadium, V = 51.2, is tri- and pentavalent. It forms five oxides, of which the highest, *vanadium pentoxide* (V₂ O₅), is the most important. When dissolved in ammonia it yields *ammonium vanadate* (N H₄ V O₃) as colourless, transparent, crystalline crusts, soluble in 100 parts of water, but almost insoluble in ammonium chloride solution. The commercial ammonium vanadate is a dirty white powder, and yields, on treatment with hydrochloric acid, a reddish-yellow solution of *vanadyl chloride* (V O Cl₃), which gives off chlorine; at the same time the solution becomes a fine blue and contains a vanadium chloride, possibly V₂ Cl₄. For practical purposes this blue solution is used and prepared in the following way:—

20 grms. (4 oz.) of ammonium vanadate in powder are mixed with
 100 grms. (20 oz.) of hydrochloric acid (34° Tw.), and
 100 grms. (20 oz.) of water.
 The mixture is heated and
 300 cc. ($\frac{5}{8}$ pint) sodium bisulphite (55° Tw.)

are added in small portions. The reduction takes place immediately.

* *Journ. Soc. Dyers and Col.*, 1890, p. 39.

Vanadium is an exceedingly active carrier of oxygen, and is used, along with chlorate of potash or soda, in printing and dyeing aniline black. Extraordinarily small quantities of vanadium are sufficient; according to Witz, this substance is still effective in a solution of 1 in 270,000; in practice 0.0012 grm. is used per litre of colour, containing 80 grms. aniline hydrochloride or $\frac{1}{61700}$ of the weight of this salt.

Cerium, Ce = 140.2, has been used for the same purpose as vanadium or copper—i.e., as a carrier of oxygen for aniline-black printing.

Cerium bisulphate, $\text{Ce}(\text{SO}_4)_2 + 3 \text{H}_2\text{O}$, in the pure state is a pink-coloured crystalline powder.

Tungsten or **Wolfram**, W = 184, is chemically related to chromium. It forms a trioxide, *tungsten trioxide*, WO_3 , which is soluble in caustic alkalies. The alkaline solution yields on addition of acids a white precipitate of *tungstic acid*, $\text{H}_2\text{WO}_4 + \text{H}_2\text{O}$. The alkaline *tungstates* are soluble in water and are crystalline. *Sodium tungstate*, $\text{Na}_2\text{WO}_4 + 2 \text{H}_2\text{O}$, crystallises in rhombic tables and is soluble in 4 parts of cold and in 2 parts of hot water; it evinces an alkaline reaction and a bitter salt-like and astringent taste. A great number of sodium polytungstates are known. By melting wolframite, tungsten ore, with soda ash a sodium tungstate (*sodium paratungstate*, $\text{Na}_{10}\text{W}_{12}\text{O}_{41}$) is obtained. It crystallises at the ordinary temperature in large triclinic crystals which contain 28 molecules of water; but at elevated temperatures with less water. It has been unsuccessfully recommended as a substitute for stannate of soda, and is sometimes added to this article to increase the effect of the stannate. Of greater importance is the application of this tungstate to make textile goods unflammable; it is especially suitable for this purpose, since it does not affect the fibre nor the colours.

Chromium tungstate, $\text{Cr}_2(\text{WO}_4)_3$, is produced by the double decomposition of an alkaline tungstate with chrome alum or chromium chloride, and is sold as a green paste, containing about 40 per cent. of dry matter. It also serves as an oxidising agent in aniline-black printing.

Uranium, U = 239, also belongs to the chromium group.

Uranium sulphate, $\text{U}(\text{SO}_4)_2 + 8 \text{H}_2\text{O}$, which crystallises in greenish rhombic crystals, has been recommended as a wool mordant,* as it yields fine grey shades with the alizarins.

Uranium salts are poisonous.

VARIOUS CHEMICALS.

Hydrogen Peroxide, $\text{H}_2\text{O}_2 = \begin{array}{c} \text{O}-\text{H} \\ | \\ \text{O}-\text{H} \end{array}$ —*Oxygenated Water*.—Hydrogen peroxide occurs in small quantities in the air and in rain

* W. M. Gardner, *Journ. Soc. Dyers and Col.*, 1890, p. 39.

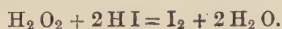
water, where it is probably produced by the action of ozone on water. It is prepared artificially by dissolving barium peroxide in acidulated water at a moderate temperature. Other peroxides—*e.g.*, those of sodium or calcium—act in the same way. The reaction proceeds according to the equation—



The barium peroxide must be used as pure as possible, and in a very finely-divided state. Purity is necessary for a high percentage yield, as the slightest impurity causes the yield to be much lessened. The barium peroxide is soaked repeatedly in water to remove any caustic barium oxide, and finally passed through a fine sieve, collected on filters, and made into a paste. For the preparation of hydrogen peroxide the paste is introduced into dilute sulphuric acid, which must be done very slowly; care must be taken that the temperature does not exceed 20° C., and the liquid must be stirred continually in order that the peroxide may never remain in contact with neutral parts of the solution; otherwise decomposition takes place immediately, and the yield suffers in consequence. When the solution is nearly neutralised it is advantageous to add sufficient phosphate of soda to replace the free sulphuric acid by phosphoric acid in the free state, since this substance has a preserving influence on the product. The liquid portion is separated from the sediment, the latter washed with water, and the wash waters are run together and made into a 3 per cent. solution, from which the dissolved baryta can be best precipitated by sodium sulphate.

Hydrogen peroxide has not been prepared in the pure state. It has been concentrated in a vacuum to a colourless, syrupy liquid of 1·45 sp. gr., which does not solidify at -30° C. It possesses a bitter, astringent taste, mixes with water in all proportions, and evaporates in *vacuo*. Very diluted aqueous solutions can be boiled without the peroxide being decomposed, a part of it escaping together with the steam.

The peroxide is very unstable in concentrated solutions, and decomposes readily with evolution of oxygen; in diluted and slightly acidulated solutions it keeps better. The decomposition takes place even at a medium temperature, and by heating it can be increased to an explosion. In consequence of this easy decomposition, and owing to the fact that oxygen is given off in the nascent state, hydrogen peroxide acts as a powerful oxidising agent. Thus chromium oxide and arsenic (the element) are converted into chromic and arsenic acids respectively, sulphides are transformed into sulphates (*e.g.*, Pb S into Pb S O₄); organic colouring matters are decolorised and destroyed; from sulphuretted hydrogen sulphur, from hydrochloric and hydriodic acids chlorine and iodine respectively are separated—for example—



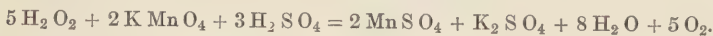
Hydrogen peroxide acts but slowly on a solution of pure potassium iodide; but iodine is separated immediately on addition of ferrous sulphate (and can be recognised by the reaction on starch paste). The oxides of barium, magnesium, and zinc are oxidised by peroxide of hydrogen into the peroxides; for instance—



H. Koechlin makes use of this fact in the bleaching of cotton.* (See p. 110.)

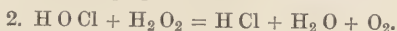
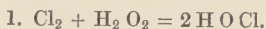
In the above cases hydrogen peroxide is an oxidising agent, but some substances are reduced by it, such as unstable oxides like the mercury, silver, and gold oxides; and certain acids such as chromic and permanganic acids.

The quantitative determination of hydrogen peroxide is based on its reaction with potassium permanganate in the presence of acids:—



From the amount of oxygen evolved the percentage of hydrogen peroxide present can be calculated.

Chlorine in aqueous solution is oxidised to hypochlorous acid and subsequently reduced to hydrochloric acid:—



Hydrogen peroxide is also resolved into water and oxygen by many substances in a finely-divided state—*e.g.*, gold, platinum, silver, carbon, or manganese peroxide.

Commercial peroxide of hydrogen forms a colourless liquid which contains about 3 per cent. $\text{H}_2 \text{O}_2$ in aqueous solution. The strength of the commercial article is expressed in volumes of available oxygen.

Hydrogen peroxide may be stored in well-tarred casks, in *bright* tin vessels, or in such which have been coated with amber varnish or in glass vessels. Since many metals have a catalytic action on the substance, decomposing it into water and oxygen, it is generally used in earthenware or wooden vessels. It should not be exposed to light or heat, and should not be stored in tightly closed vessels, else these might be broken by inside pressure from evolved oxygen.

Hydrogen peroxide is the best bleaching agent known for all classes of fibres. Owing to its high price its application was restricted until recently to the bleaching of tussur-silk and feathers; but it is now used in increasing quantities for the bleaching of woollen goods. The practical application has been described under *Bleaching*.

Carbon Bisulphide, CS_2 , is produced by passing vapours of sulphur over red-hot charcoal. It is a colourless liquid, usually possessing a peculiar, very disagreeable smell, is very volatile, and boils at 47°C . It has a specific gravity of 1.297 at 0° and is almost insoluble

* Prudhomme, *Journ. Soc. Dyers and Col.*, 1891, p. 136.

in water, but is miscible with alcohol and ether. It is very inflammable.

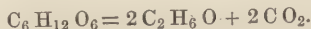
Carbon bisulphide is an excellent solvent for sulphur, phosphorus, fatty oils, resins, gums, and caoutchouc.

Petroleum Spirit, Petroleum Benzene, and Ligroïn, are the light oils of American petroleum, and consist chiefly of the saturated hydrocarbons of the fatty series, which correspond to the general formula $C_n H_{2n+2}$. They possess a specific gravity of 0.65 to 0.75, and boil from 50° to 120°; the lightest of these oils are called petroleum-spirit, the heaviest ligroïn.

Methyl Alcohol or Wood Spirit, $C H_3 (O H)$, is produced by the destructive distillation of wood. It is a colourless, mobile liquid, possessing a pure spirituous smell; the specific gravity is 0.796 at 20° C. and the boiling point 66°. It burns with a non-luminous flame, and is miscible with water, alcohol, and ether. Mixtures of methyl-alcohol and water possess nearly the same specific gravities as those of ordinary alcohol and water.

Methyl alcohol strongly resembles ethyl alcohol.

Ethyl Alcohol or Ordinary Alcohol (*Spirits of Wine*), $C_2 H_5 (O H)$, is the product of the vinous fermentation of sugar:—



Pure alcohol, free from water, is called *absolute alcohol*; it is a colourless, mobile liquid, possessing a pleasant spirituous smell and a burning taste. Its specific gravity is 0.789 at 20° C.; and it boils at 78°.3. Alcohol absorbs water from the air with avidity; and mixes with water in all proportions, heat being evolved, and contraction taking place. It cannot be completely separated from water by distillation; to withdraw all the water the liquid must be distilled with a substance capable of combining with water, such as quicklime or potassium carbonate.

Alcohol is very inflammable, burning with a slightly luminous blue flame. It dissolves many mineral salts, the caustic alkalies, the carbonates, resins, fatty acids, and a great many other carbon compounds. Most gases dissolve more freely in alcohol than in water. Some salts, such as calcium chloride or magnesium nitrate, form crystalline compounds with alcohol, which plays in them the part of water of crystallisation.

Alcohol is converted by oxidising agents, such as manganese peroxide and sulphuric acid, chromic acid, finely-divided platinum and air into *aldehyde*, $C_2 H_4 O$ (*alcohol dehydrogenatus*), and into acetic acid.

The *proof spirit* of the excise contains 50.8 parts by weight of alcohol and 49.2 of water, and possesses a specific gravity of 0.920 at 15.5°.

Methylated spirit is exempted from excise duty. It contains chiefly ethyl alcohol, as also methyl alcohol and other substances, such as resins, to make it unfit for drinking. Manufacturers can obtain it for industrial purposes without the addition of non-volatile substances.

By a recent order of Council, methylated spirit will in future contain in addition to methyl alcohol, one third per cent. of mineral naphtha.

SPECIFIC GRAVITY OF ETHYL-ALCOHOL AND PERCENTAGE
BY WEIGHT AT 60° F. (15½° C.)—(Fownes).

Specific Gravity.	Per cent. by weight C ₂ H ₆ O.	Specific Gravity.	Per cent. by weight C ₂ H ₆ O.	Specific Gravity.	Per cent. by weight C ₂ H ₆ O.
0.9991	0.5	0.9511	34	0.8769	68
0.9981	1	0.9490	35	0.8745	69
0.9965	2	0.9470	36	0.8721	70
0.9947	3	0.9452	37	0.8696	71
0.9930	4	0.9434	38	0.8672	72
0.9914	5	0.9416	39	0.8649	73
0.9898	6	0.9396	40	0.8625	74
0.9884	7	0.9376	41	0.8603	75
0.9869	8	0.9356	42	0.8581	76
0.9855	9	0.9335	43	0.8557	77
0.9841	10	0.9314	44	0.8533	78
0.9828	11	0.9292	45	0.8508	79
0.9815	12	0.9270	46	0.8483	80
0.9802	13	0.9249	47	0.8459	81
0.9789	14	0.9228	48	0.8434	82
0.9778	15	0.9206	49	0.8408	83
0.9766	16	0.9184	50	0.8382	84
0.9753	17	0.9160	51	0.8357	85
0.9741	18	0.9135	52	0.8331	86
0.9728	19	0.9113	53	0.8305	87
0.9716	20	0.9090	54	0.8279	88
0.9704	21	0.9069	55	0.8254	89
0.9691	22	0.9047	56	0.8228	90
0.9678	23	0.9025	57	0.8199	91
0.9665	24	0.9001	58	0.8172	92
0.9652	25	0.8979	59	0.8145	93
0.9638	26	0.8956	60	0.8118	94
0.9623	27	0.8932	61	0.8089	95
0.9609	28	0.8908	62	0.8061	96
0.9593	29	0.8886	63	0.8031	97
0.9578	30	0.8863	64	0.8001	98
0.9560	31	0.8840	65	0.7969	99
0.9544	32	0.8816	66	0.7938	100
0.9528	33	0.8793	67		

Amyl Alcohol or **Isobutyl Carbinol** (*Fusel Oil*), C₅ H₁₁ (O H), is the chief constituent of fusel oil, obtained in the rectification of potato spirit. It is a colourless liquid, possessing a peculiar, penetrating smell; it dissolves in alcohol and ether, but is not miscible with water; one part only dissolves in 50 parts of water. The specific gravity is 0.8104 at 20° C., and the boiling point 132°. It yields on oxidation valeric acid. In its chemical properties amyl alcohol resembles ordinary alcohol.

Ether or **Sulphuric Ether**, (C₂ H₅)₂ O, is produced by heating a mixture of alcohol and sulphuric acid to 140° C. It is a colourless, very mobile liquid, possessing a strong and peculiar ethereal smell. It

does not mix with water, but does so, in all proportions, with alcohol; it dissolves in 10 parts of water. The specific gravity is 0.736 at 0° C. and the boiling point 35°. It evaporates rapidly at the ordinary temperature; and is very inflammable, burning with a non-luminous flame. When mixed with air it explodes, and, from its low boiling point, great care must be taken to avoid explosions.

Many organic compounds, notably hydrocarbons, fats, oils, and resins, readily dissolve in ether.

Glycerin, $C_3H_5(OH)_3$, is contained in most fats and fatty oils of the vegetable and animal kingdoms, and is formed in small quantities by the alcoholic fermentation of sugar. It is produced as a bye-product in the manufacture of soap and of stearin. Glycerin is a colourless syrupy liquid, which possesses a very sweet taste. It is very soluble in water and in alcohol, but insoluble in ether, and, when anhydrous, absorbs water from the air with avidity. It has a specific gravity of 1.265 at 15° C. It boils at the ordinary pressure at 290° with slight decomposition, and can be distilled without being decomposed at a reduced pressure, or in the presence of aqueous vapour.

Glycerin is a trivalent alcohol, and resembles ethyl alcohol in many respects. It dissolves the alkalis, alkaline earths, and many metallic oxides, probably forming compounds analogous to alcohol. It forms ethers with the inorganic and organic acids, the most important of which are the glycerin ethers of palmitic, stearic, and oleic acid, which have been described in connection with the acids.

Glycerin is added on account of its hygroscopicity to print-colours, finishing materials, &c., to prevent them from drying.

Acetin is a mixture of the acetic ethers of glycerin (mono-, di-, and tri-acetin), and is produced by boiling glycerin with glacial acetic acid. It is a solvent for some dyestuffs, *e.g.*, the insoluble indulines, and is used for this purpose in calico-printing.

Olive Oil.—Olive oil is produced from olives, the fruit of the olive tree, (*Olea Europæa*, Linn.), which is grown in southern countries. The ripe olives are ground to a pasty mass and pressed. The oil obtained from the first pressing—the so-called virgin oil (*huile vierge*)—is the best, and is used chiefly as an edible oil. After the first pressing the material still retains much oil; it is treated with hot water and pressed once more. The oil obtained from the second pressing has a fine yellow colour, but it is more prone to become rancid than the virgin-oil. It is used for Turkey-red dyeing (*huile tournante*), and for oiling wool before spinning (*huile lampante*). By a third pressing an inferior oil is obtained, which is used for soap-making.

Olive oil consists chiefly of the tri-glycerides of oleic acid, palmitic acid, and stearic acid, containing about 72 per cent. of olein, and 28 per cent. of palmitin and stearin.

The specific gravity of different oils varies from 0.914 to 0.917, but it rises to 0.920, and even to 0.925, in the case of hot-pressed oils

which contain more palmitin or stearin. The oil becomes turbid at $+2^{\circ}\text{C}.$, and at -6° deposits 28 per cent. of palmitin and stearin.

Olive oil, when exposed to the air, decomposes into free acid and glycerin, and becomes rancid:—



It thus acquires a disagreeable smell and taste and an acid reaction. It is decomposed in the same way by the action of steam or by boiling with acids or caustic alkalies; in the last case salts of the acid are formed. At the ordinary temperature alkalies do not decompose the oil, although they form an emulsion with it (see below). *Gallipoli oil* or *emulsive oil* (*huile tournante*) is olive oil which contains free acids by having become rancid.

When olive oil is shaken well with a dilute solution of sodium carbonate a white milky liquid or an *emulsion* is formed; after some time two layers separate, one containing the oil, the other containing the aqueous liquid. If the oil contains free fatty acids they form a salt or "soap" with the caustic lye, and the presence of this soap tends to make the emulsion more permanent. The emulsion is merely a mechanical mixture of those parts of the oil which are insoluble in alkaline water (the undecomposed glycerides) with the caustic lye and the soluble products of decomposition (soaps). The oil exists in the emulsion in a state of the finest division, in which form it is particularly well absorbed by the cotton fibre. For this reason emulsive oil is extensively used in Turkey-red dyeing; the methods of application and the chemical reactions taking place in the fibre will be given under that heading. In calico-printing olive oil is used as an admixture to the printing colour for the purpose of making the paste smooth and free from air-bubbles. In silk dyeing it is largely used for softening the material after dyeing.

Castor Oil.—The seeds of *Ricinus communis* contain 40 to 45 per cent. of oil, which consists principally of triricinolein, the triglyceride of ricinoleic acid, together with some stearin and palmitin.

Castor oil is a colourless liquid which possesses when fresh a mild, and afterwards an irritating taste; it is very viscous, and when exposed to the air gradually thickens to a tough mass. It does not dry completely, even in thin layers. The specific gravity is 0.960 to 0.964 according to Allen or 0.9613 to 0.9736 according to Valenta. It becomes solid between -10° and $-18^{\circ}\text{C}.$

Pure castor oil mixes in all proportions with absolute alcohol and glacial acetic acid; it dissolves in two parts of alcohol of 90 per cent. strength, and four parts of alcohol of 84 per cent., but is insoluble in petroleum spirit.

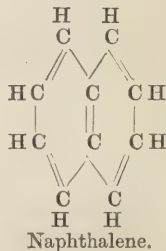
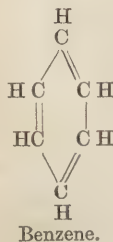
Castor oil is saponified analogously to olive oil, the chief product being ricinoleic acid.

Linseed Oil is obtained from the seeds of flax, *Linum usitatissimum*. It has a light yellow, or if obtained by hot pressing, a brownish-yellow

colour and a peculiar smell and taste. The specific gravity at 15°C . is 0.930 to 0.935; it solidifies slowly at -16° to -27° . In the air it absorbs oxygen and soon becomes rancid and thick, drying in thin layers to a neutral substance which is insoluble in ether. It is adulterated with fish oil, rape oil, hemp-seed oil, and cameline oil.

Linseed oil is chiefly used by painters on account of its property of drying and forming a varnish. For the same reason it is used in cotton-velvet dyeing. Prussian blue and other colours are mixed in a finely-ground state with linseed oil and painted on the velvet with brushes, in order to give it colour and a fine gloss.

Compounds of the Aromatic Series.—The aromatic hydrocarbons and their derivatives contain relatively less hydrogen than those of the fatty series. All the aromatic compounds contain a group of 6 carbon atoms, in which 18 of the carbon bonds are taken up by union of carbon with carbon, whilst 6 remain open to saturation. These 6 valencies are saturated with hydrogen in *benzene* (C_6H_6), while a large number of other substances are formed by one or more atoms of hydrogen being substituted by other atoms or more or less complicated groups (radicals). It is supposed that the 6 carbon atoms in benzene are combined in a ring as shown by the first diagram (on the left):—



A diagram, with or without numbers, is generally used, in which each corner signifies an atom of carbon; if an atomic symbol is placed next to the corner the carbon atom is combined with the same; otherwise the carbon atom is combined with hydrogen. The third diagram, for instance, indicates chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$). If more than one atom of hydrogen is replaced by other elements or radicals, different compounds are obtained if the substituted groups are in relatively different positions; for instance, the dichlorobenzenes, the chlorine atoms of which are placed either in the positions 1 and 2, or in 1 and 3, or in 1 and 4, are different. Diagrams like those above are also used for demonstrating the constitution of naphthalene and its derivatives.

Use will be made of these diagrams as brief indicators of the constitution of the undermentioned compounds:—

Ortho-compounds are those which contain the substituting groups

in the position 1 : 2 (or 2 : 3, or 4 : 5, &c.); metacompounds are substituted in 1 : 3 (or 2 : 4, or 3 : 5, &c.); paracompounds in 1 : 4 (or 2 : 5, or 3 : 6). The *alpha* positions in naphthalene and its derivatives are 1, 4, 5, and 8, the *beta* positions are 2, 3, 6, and 7.

Benzene, C_6H_6 , is one of the products of the destructive distillation of coal, and occurs in coal tar. It is a colourless, mobile liquid, possessing an ethereal smell, and having a specific gravity of 0.8799 at 20° C.; it solidifies at about 0°, melts at 8°, and boils at 80°.5. It is very inflammable, and burns with a smoky flame. It is not miscible with water, but mixes in all proportions with alcohol and ether. It dissolves very freely sulphur, phosphorus, fats, and resins.

Toluene, C_7H_8 , is associated with, and has a strong resemblance to, benzene. Specific gravity 0.8656 at 20° C., and boiling point 110°.3.

Naphthalene, $C_{10}H_8$, also occurs in coal tar. It crystallises and sublimes in colourless glittering laminae; melts at 79° C. and boils at 218°. It is very volatile, and possesses a peculiar smell. It is insoluble in water, sparingly soluble in cold alcohol, and freely soluble in ether or hot alcohol. It evolves enormous quantities of dense black smoke when burning in the air.

Anthracene, $C_{14}H_{10} = C_6H_4 \begin{array}{c} \diagup CH \\ | \\ CH \diagdown \end{array} C_6H_4$, is also found in coal

tar. It crystallises in colourless monoclinic tablets, having a blue fluorescence. It melts at 213° C., and boils somewhat above 360°. It is sparingly soluble in alcohol and ether, but readily soluble in hot benzene.

Phenol (*Carbolic Acid*), $C_6H_5(OH)$, occurs in coal tar. It forms, in the pure state, a colourless crystalline mass, which becomes gradually reddish, and is deliquescent in the air; it melts at 42° C. and boils at 183°; the specific gravity is 1.084 at 0°. It possesses a peculiar smell and a burning taste, is very poisonous, and is antiseptic. It dissolves in 15 parts of water at 20°; and very freely in alcohol, ether, and glacial acetic acid. The neutral solutions of phenol are coloured violet by ferric salts; bromine water precipitates tribromophenol from solutions, even when highly diluted. Phenol forms salts with metallic bases, such as sodium phenolate (C_6H_5ONa); the salts are decomposed by the weakest acids, even by carbonic acid. Phenol dissolves readily in caustic soda, forming the phenolate or phenate of soda.

Cresol or *Oxytoluene*, $C_6H_4(CH_3)(OH)$.—Ortho-, meta-, and para-cresol are known.

Resorcin, or *Metadioxybenzene*, $C_6H_4(OH)_2$; ($OH = 1 : 3$), forms colourless crystals, easily soluble in water and in alkalis.

Alphanaphthol, $C_{10}H_7(OH)$; ($OH = 1$), is obtained from naphthalene by fusing alphanaphthalene monosulphonic acid with caustic soda. It crystallises in colourless, glittering needles, melts at 95° C.,

boils at 278° to 280° , and has a phenolic smell. It is sparingly soluble in hot water, freely in alcohol and ether. Ferric chloride produces a violet precipitate in the aqueous solution. Alphanaphthol, like phenol, forms salts (*naphtholates*), and dissolves in caustic soda.

Betanaphthol, $C_{10}H_7(OH)$; $(OH:2)$, is obtained analogously to alphanaphthol by fusing betanaphthalene monosulphonic acid with caustic soda. It crystallises in colourless, glittering laminæ, melts at $122^{\circ}C$, and boils at 286° . It is sparingly soluble in hot water, readily in alcohol and ether. The aqueous solution becomes greenish on addition of ferric chloride. Betanaphthol also resembles the phenols in forming salts (*naphtholates*), and dissolves in caustic soda.

The *azo-compounds* of betanaphthol are essentially different from those of alphanaphthol. They possess in the non-sulphonated state a slightly basic character, and contain no hydroxyl group, not being soluble in caustic soda.

Dioxynaphthalenes, $C_{10}H_6(OH)_2$.—A great number of these are known.

Aniline (*Amido-Benzene*), $C_6H_5NH_2$.—Aniline was discovered in 1826, by Unverdorben; he obtained it by the dry distillation of indigo and called it *crystalline*. Runge found it in 1834 in coal tar and named it *kyanol*. Zinin prepared it first from nitrobenzene in 1842, and described it as *benzidame*. The name *aniline* (from *anil*, Span. = indigo) was proposed by Fritsche, who prepared it in 1840 from indigo by means of caustic potash. A. W. Hofmann found in 1843 that the various products were identical. Aniline was manufactured on the large scale only after Perkin's discovery of mauve in 1856.

For the production of aniline benzene is converted into nitrobenzene ($C_6H_5NO_2$) by treatment with nitric and sulphuric acid; and the product is reduced with hydrochloric acid and iron. Aniline is a colourless oil having a peculiar smell and a strong power of refracting light. It soon becomes brown under the influence of light and air. It solidifies in a freezing mixture and melts again at $-8^{\circ}C$, boils at 182° ; it volatilises freely with steam. The specific gravity is 1.0265 at 15° , 1.024 at 17.5° and 1.0195 at 20° (for practical calculations = 1). It has a light aromatic smell and a burning taste. The vapours of aniline when inhaled are poisonous and cause a specific dangerous illness (*anilisme*) which is not uncommon in aniline works. The oil when taken internally is also poisonous.

One part of aniline is soluble in 31 parts of water at 12.5° ; it dissolves in all proportions in a 50 per cent. solution of aniline hydrochloride in water, and aniline hydrochloride generally increases the solubility of aniline in water. Aniline is readily soluble in most of the usual solvents and is itself a good solvent for many substances, such as sulphur, phosphorus, indigo, aniline-blue, and camphor, but not for caoutchouc. It burns with a smoky flame. Aniline is readily

affected by chemical agents. It undergoes many changes by oxidation under different conditions which are very important in the production of dyestuffs and in dyeing.

Commercial aniline.—The purest product is *aniline for blue*, which consists of almost pure aniline. The other brands, such as “aniline for red” contain varying quantities of homologous bases, chiefly ortho- and paratoluidine.

Aniline is a monacid base and forms well-defined salts, which readily crystallise. Aniline and its hydrochloride are used by dyers chiefly for the production of aniline black.

Aniline hydrochloride, $C_6H_5NH_2 \cdot HCl$, is the most important salt of aniline, and is sold in large quantities under the name *aniline salt*. It crystallises in large leaf-shaped white crystals which become coloured in the air from grey to black; it is freely soluble in water and in alcohol, melts at 192° , and volatilises without decomposition.

Aniline sulphate, $(C_6H_5NH_2)_2 \cdot H_2SO_4$, is sparingly soluble in water and in alcohol, but insoluble in ether. An unstable acid sulphate $(C_6H_5NH_2 \cdot H_2SO_4)$ has also been prepared.

Toluidines, $C_6H_4(CH_3)NH_2$.—Three isomeric toluidines are known, which strongly resemble aniline; they are obtained by the reduction of three different nitrotoluenes. By the action of nitric acid on toluene, chiefly ortho- and paranitrotoluene are obtained, which yield on reduction a mixture of ortho- and paratoluidine.

Orthotoluidine is a colourless oil which boils at 197° to $197.5^\circ C.$ and has a specific gravity of 1.0037 at 15° .

Metatoluidine is a colourless oil which boils at $197^\circ C.$ It occurs in small quantities only in the commercial products and has no practical value owing to its high cost.

Paratoluidine forms colourless crystals, which melt at $45^\circ C.$ and boil at 198° .

Alphanaphthylamine, $C_{10}H_7NH_2$; $(NH_2 : 1)$, is obtained by reducing alphanitronaphthalene, the product of the reaction of nitric acid on naphthalene. It forms colourless crystals, which melt at $50^\circ C.$, and boils at 300° . It is almost insoluble in water, but freely soluble in alcohol or ether. The commercial product has a reddish-grey to brown colour and a very disagreeable smell. It should dissolve in hot diluted acids without leaving much insoluble oil. Mild oxidising agents produce a blue precipitate in the solutions of alphanaphthylamine salts. Alphanaphthylamine resembles aniline chemically. It is a monacid base and forms crystalline salts which are not very soluble in water.

Betanaphthylamine, $C_{10}H_7NH_2$; $(NH_2 : 2)$, is prepared by heating betanaphthol with ammonia. It forms colourless inodorous laminæ, melts at 112° and boils at 294° . It is sparingly soluble in cold but freely soluble in hot water, alcohol, and ether. The commercial product is very pure and forms a fused pink-coloured mass.

Betanaphthylamine is a monacid base and forms crystalline salts. The hydrochloride ($C_{10}H_7N \cdot HCl$) is fairly soluble in water.

The constitution of a number of compounds mentioned in the description of the dyestuffs is indicated below.

Salicylic acid or orthophenolcarboxylic acid, $C_6H_4(OH)(CO_2H)$. (1 : 2).

Cresoxylic acid or orthocresolcarboxylic acid, $(C_6H_3)(CH_3)(OH)(CO_2H)$. (1 : 2 : 3).

Alphanaphthol sulphonic acid (Cl), $(C_{10}H_6)(OH)(SO_3H)$, is the compound obtained from alphanaphthylamine sulphonic acid (L) (see below).

Alphanaphthol sulphonic acid (N W), $(C_{10}H_6)(OH)(SO_3H)$, is obtained from naphthionic acid, and was first prepared by Neville and Winther.

Alphanaphthol disulphonic acid (Sch.), $C_{10}H_5(OH)(SO_3H)_2$; (OH : 1, SO_3H : 4 and 8), was discovered by Mensching and patented by the Schoellkoff Aniline Co.

Alphanaphthol epsilon disulphonic acid, $C_{10}H_5(OH)(SO_3H)_2$; (OH : 1; SO_3H : 3 and 8) was discovered by Andresen and patented by the Berlin Aniline Co.

Betanaphthol (mono) sulphonic acid (S), $C_{10}H_6(OH)(SO_3H)$; (2 : 6), was discovered by Schaeffer and is known as Schaeffer's acid.

Betanaphthol (mono) sulphonic acid (B), or betanaphthol alphasulphonic acid, $C_{10}H_6(OH)(SO_3H)$; (2 : 8), was discovered by Rumpf and patented by the Elberfeld Colour Works (Bayer).

Betanaphthol (mono) sulphonic acid (F), $C_{10}H_6(OH)(SO_3H)$; (2 : 7), the so-called "F acid," was patented by L. Cassella & Co.

Betanaphthol disulphonic acid R (R. Salt), $C_{10}H_5(OH)(SO_3H)_2$; (OH : 2, SO_3H : 3 and 6) was discovered by Baum and patented by M. L. B.

Betanaphthol disulphonic acid G (G Salt; Gamma acid), $C_{10}H_5(OH)(SO_3H)_2$; (OH : 2, SO_3H : 6 and 8), was patented by the Hoechst Colour Works (M. L. B.)

Betanaphthol delta disulphonic acid, $C_{10}H_5(OH)(SO_3H)_2$; (OH : 2; SO_3H : 3 and 7), is obtained from "F acid" and was patented by L. Cassella & Co.

Xylidine, $C_6H_3(CH_3)_2NH_2$.—The commercial article is a mixture of isomeric compounds.

Cumidine, $C_6H_2(CH_3)_3NH_2$.

Anisidine, $C_6H_4(OCH_3)NH_2$.

Phenitidine, $C_6H_4(OC_2H_5)NH_2$.

Amidoazobenzene, $C_6H_5N_2C_6H_4NH_2$.

Amidoazotoluene, $C_6H_4(CH_3)N_2C_6H_3(CH_3)NH_2$.

Phenylene diamine, $C_6H_4(NH_2)_2$.

Toluylene diamine, $C_6H_3(CH_3)(NH_2)_2$.

Naphthylene diamine, $C_{10}H_6(NH_2)_2$.

Benzidine, $(C_6H_4NH_2)_2 = H_2N-C_6H_4-C_6H_4-NH_2$.

Tolidine $(C_6H_3(CH_3)NH_2)_2$.

Dianisidine $(C_6H_3(OC_6H_5)NH_2)_2$.

Ethoxybenzidine, $H_2N-C_6H_4-C_6H_3(OC_2H_5)-NH_2$.

Diamido azoxytoluene, $H_2N-C_6H_3(CH_3)-N \underset{\text{O}}{\underset{\text{O}}{\text{N}}}-C_6H_3(CH_3)NH_2$.

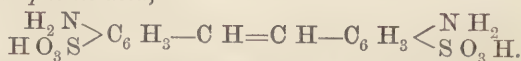
Diamidocarbazol, $C_{12}H_7N(NH_2)_2$.

Benzidinesulphone, $\begin{array}{c} C_6H_3-NH_2 \\ | \\ C_6H_3-NH_2 \end{array} \begin{array}{c} > S O_2 \\ > S O_2 \end{array}$.

Sulphanilic acid or *para* amido benzene sulphonic acid, $C_6H_4(NH_2)SO_3H$.

Metanilic acid or *meta* amido benzene sulphonic acid, $C_6H_4(NH_2)SO_3H$.

Diamidostilbene disulphonic acid,



Naphthionic acid, $C_{10}H_6(NH_2)(SO_3H)$; (1 : 4), is the *alpha* sulphonic acid of alphanaphthylamine discovered by Piria, which is prepared by heating alphanaphthylamine sulphate (*Neville and Winther*).

Alphanaphthylamine sulphonic acid (L), $C_{10}H_6(NH_2)(SO_3H)$; (1 : 5), was discovered by Laurent.

Alphanaphthylamine disulphonic acid, $C_{10}H_5(NH_2)(SO_3H)_2$, prepared by the action of fuming sulphuric acid on alphanaphthylamine, is a mixture of several compounds.

Betanaphthylamine alpha sulphonic acid, $C_{10}H_6(NH_2)(SO_3H)$; (2 : 8), was patented by the Badische Aniline and Soda Fabrik (B. A. S. F.).

Betanaphthylamine beta sulphonic acid, $C_{10}H_6(NH_2)(SO_3H)$; (2 : 6), or *betanaphthylamine sulphonic acid (Br.)*, was discovered by Prinz and patented by Broenner's Colour Works.

Betanaphthylamine gamma sulphonic acid, $C_{10}H_6(NH_2)(SO_3H)$; (2 : 5), or *betanaphthylamine sulphonic acid (D)*, was patented by Dahl & Co.

Betanaphthylamine delta sulphonic acid, $C_{10}H_6(NH_2)(SO_3H)$; (2 : 7), or *betanaphthylamine sulphonic acid (F)*, or *delta-acid*.

Betanaphthylamine disulphonic acid (R), $C_{10}H_5(NH_2)(SO_3H)_2$ ($NH_2 : 2, SO_3H : 3$ and 6) (*amido R acid*), is produced by the action of ammonia on R salt.

Betanaphthylamine disulphonic acid (G), $C_{10}H_5(NH_2)(SO_3H)_2$ ($NH_2 : 2, SO_3H : 6$ and 8) (*amido G acid*), is produced by the action of ammonia on G salt.

Gamma amido naphthol sulphonic acid, $C_{10}H_5(NH_2)(OH)(SO_3H)$; ($NH_2 : 2, OH : 8, SO_3H : 6$), is produced by heating amido G acid with caustic soda.

1 : 8 *Dioxynaphthalene sulphonic acid*, $C_{10}H_5(OH)_2(SO_3H)$; ($OH : 1$ and $8, SO_3H : 4$), is obtained by heating alphanaphthol disulphonic acid, Sch, with caustic soda.

PART VI.

NATURAL COLOURING MATTERS.

INDIGO.

INDIGO has long been regarded as one of the most valuable and important of all colouring matters. It was used in India and Egypt long before the Christian era. It was introduced into Europe in the sixteenth century, but for a great many years very little was used on account of the opposition of the woad cultivators, who induced the English, French, and German governments to prohibit its use. The cultivators of woad contended that indigo was not only a fugitive dye, but that it was a corrosive and pernicious drug. In reality they feared that the importation of indigo would ruin their trade in woad. In France the law was so severe that Henry IV. issued an edict condemning to death anyone who used that "pernicious drug," which was called the "devil's food." It is only since the year 1737 that the French dyers have had the right to use indigo without restriction. In England the statute prohibiting the use of indigo has never been repealed.

By far the greatest amount of indigo is obtained from India, and more especially from Bengal, Oude, and Madras. It is also manufactured in Java, Manilla, China, Japan, Central America, Brazil, and certain parts of Africa. The principal plants cultivated for the manufacture of this dye are the *Indigofera tinctoria*, *Indigofera anil*, *Indigofera disperma*, and *Indigofera argentea*. There are numerous other varieties of lesser importance.

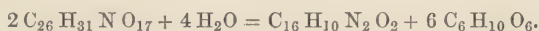
Indigo may be obtained from other plants besides the species of *Indigofera*, but in much smaller quantities. The most important is the woad plant, or *Isatis tinctoria*, which was formerly very extensively cultivated in England and on the continent for blue dyeing. It is still grown in Lincolnshire and on the Continent (in the South of France, Hungary, &c.), but is now never used alone for dyeing. *Isatis tinctoria* is a biennial plant. The leaves are gathered in the second year, made into a paste with water, allowed to ferment for about

fifteen days in heaps, and then dried. The product is known as woad, and is used in the woad-vat along with indigo.

The principal colouring matter of indigo is *indigotin* or indigo-blue. It also contains *indirubin* or indigo-red, indigo-brown, indigo-gluten, water, and mineral matter.

Indican.—The plant from which indigo is obtained, does not contain any colouring matter ready formed, but it probably contains a glucoside, which, under certain conditions, splits up into indigo and a kind of sugar. It was formerly supposed that the indigo existed in the plant in the form of indigo-white held in solution by the vegetable fluids, but this theory has been proved to be incorrect. The juices of plants have an acid reaction, whereas indigo-white or reduced indigo is only soluble in alkaline liquids. The glucoside, which was first isolated by Schunck, is named *Indican*. It forms a brown, transparent, uncrystallisable syrup, having the formula $C_{26}H_{31}NO_{17}$. It evolves ammonia on boiling with caustic soda.

By the action of boiling dilute acids, the indican is split up into indigotin and indiglucin, a kind of sugar. The change may be represented by the following equation:—



A similar reaction is supposed to occur during the fermentation process in the manufacture of indigo. Indican is very susceptible of alteration, and its modifications, when treated with dilute acids or when acted upon by ferments, yield indirubin, indigo-brown, &c.

Manufacture of Indigo.—The *Indigofera tinctoria* is the plant most abundantly cultivated. It is herbaceous, growing to a height of 3 to 4 feet, and having a single stem, about half an inch in diameter.

The land is ploughed in October or November, and the seed sown towards the end of March or beginning of April. About 30 lbs. of seed are required per acre. A light loam is the best kind of soil, and sunshine, with occasional light showers, is most favourable to the growth of the plant. The crop is frequently considerably damaged by long-continued rain. The plant grows rapidly, and attains a height of about 3 feet. It is cut for the first time from the middle of June to the beginning of July, varying according to the quality of the soil and the state of the weather. It is important to cut the plants just when mature, indicated by the bursting forth of the flower buds and the expansion of the blossoms. After two months the plants are cut a second time, but the yield of indigo is not so good as that obtained from the first crop.

There are two methods in general use for the treatment of the plants.

I. *From the Fresh Leaves.*—In Bengal the factories usually contain two rows of vats, built of brickwork, and lined with stone and cement, the bottom of the one row being nearly upon a level with the top of the other. There are from ten to twenty vats in each series, the area

of each vat being about 400 square feet and the depth about 3 feet. The lower vats, however, are often one-third longer than the upper vats. The cut indigo plants, tied up in bundles, are neatly placed in the upper tanks, care being taken to pack them tightly, since it is important, in order to ensure the proper degree of fermentation, that there should be left as little space as possible. The bundles are kept in position, and prevented from floating by wedging stout beams of timber across the tank. Water, which should be clear and of good quality, is then run in so as to completely cover the plants. An active fermentation, more or less rapidly, commences, lasting on an average from ten to fifteen hours, according to the temperature of the air, the quality of the water, and the ripeness of the plant. A few hours after the immersion of the plant, the condition of the vat must from time to time be carefully examined. If the fermentation is still very rapid, the vat must not be disturbed, but when it becomes more tranquil, it is an indication that the maceration of the plant is complete. Other indications of this point having been attained are the following:—(1) When the water, which was at first clean, begins to become muddy and acquire a slight greenish tinge; (2) When bubbles of a greenish colour rise to the surface here and there; (3) When towards the edge of the vat some mucilage, or a kind of greyish scum, commences to be formed; (4) When a very slight purple pellicle is observed on the surface of the liquor, especially near the corners of the vat; (5) When the liquor begins to exhale a slight but not disagreeable odour of herbs. The liquor is now run off from the steeping into the lower or beating vats. If the liquor is of a pale yellow tint, the product obtained from it will be much richer in quality, but not so abundant as if it had a golden-yellow colour. The average temperature of the liquor at this period is 30° C. From ten to eighteen men enter each vat and beat up the liquor with oars* or shovels 4 feet long, keeping up the agitation from 1½ to 3 hours. The yellow liquor gradually becomes green, and finally separates and precipitates in flakes. It is of importance that this process should be broken off at the right moment, for if it be continued too long, the precipitate formed at first will redissolve and be lost. After the beating process, the liquor is allowed to stand for two or three hours, and as the indigo subsides the supernatant liquid, which must be clear, is withdrawn. The blue pulpy mass is now collected in a separate vessel, and pumped up into a caldron of water and boiled. The principal object in boiling is to prevent a second fermentation, which would give rise to the formation of a brown resinous body, but at the same time it frees the indigo from a worthless yellow colouring matter. After standing for twenty hours, it is again boiled for from three to four hours. From the boiler the mixture is run on to a large filter called the *dripping vat*, which, for a factory containing twelve pairs of preparation vats, is 20 feet long, 10 feet wide, and 3 feet deep,

* This operation is now in many factories done by machinery.

having a false bottom 2 feet under the top edge. A thick woollen cloth or strong canvas is stretched along the bottom of the inner vessel, upon which the indigo collects as a bluish, black pasty mass. After allowing the liquid to drain for about twenty-four hours, the magma is placed into wooden boxes perforated with holes, and lined with strong cotton cloth. The pasty indigo is then submitted to a gradually increasing pressure until no more liquid runs out at the bottom. The pressure having been withdrawn, the boxes are opened and the blocks of indigo cut up, by means of a knife or brass wire, into pieces of a cubical shape, usually measuring 3 inches each way. These cubes are then taken to the drying-house, where they are placed on trellises covered with matting so as to admit of a free passage of air. Direct sunlight is carefully excluded, and care is taken not to dry the indigo too rapidly. Each fermenting vat yields from 36 to 50 lbs. of indigo.

II. *Indigo from Dried Leaves.*—The ripe plant is cut in dry weather an hour or two before sunset, and then dried in the sun on two consecutive days between 9 a.m. and 4 p.m. When dry, the plants are submitted to a process of threshing, so as to separate the leaves from the stems. The leaves in the course of a few weeks undergo a change in colour; their beautiful green tint turning a pale bluish-grey. The leaves are now ready for extraction. They are put into a steeping vat with six times their bulk of water, and allowed to macerate for two hours, with continual stirring, till all the floating leaves sink. The fine green liquor is then drawn off into the beating vats without delay, and treated as in the process previously described.

Of late years several patents have been granted in India for improvements in the manufacture of indigo. A new process, worked out by Michea is in the hands of a company known as *The Indigo Company, Limited*. It claims to effect the complete separation and conversion of the indican present in the *Indigofera*, &c., into indigotin, by the action of ammonia or other alkalies, and by more powerful means of oxidation. Two methods of treatment are described, named respectively the "cold" and the "boiling" water process.

I. *The Cold-water Process.*—The indigo plant is steeped in vats with water at its normal temperature, and the same length of time given as is usually allowed in the ordinary process of manufacture. The liquor is then drawn into the lower or beating vats, when the fermentation is either stopped or reduced to an insensible point. The temperature of the liquor is now rapidly raised by means of steam pipes to 96° F., whereby the portion of the glucoside, which has escaped decomposition in the fermentation vat, is entirely converted and rendered available for the production of indigo-blue. Ammonia is added to the liquid in quantities up to 250 lbs. of liquor ammoniæ (sp. gr. 0.880) per 1000 cubic feet of pressed plant. The amount required to be added varies according to the quality of the plant, the soil on which it is grown, and the temperature of the external air.

A solution of nitrate of potash or soda in the proportion of five pounds or more of the salt per 1000 cubic feet of plant is then added to the vat, and the beating or oxidation process is carried on as rapidly and effectually as it can possibly be done, without causing too violent a disturbance in the liquor. This is effected by employing one or more of the following devices:—

“(a.) By having beating vats of more than double the ordinary area, so as to expose a greater surface of liquid to the air.

“(b.) By having double the number of vat beaters usually employed.

“(c.) When the liquor is to be beaten by means of mechanical power, only that machinery is employed which causes the greatest exposure of the liquid to the air, and which does not produce too violent a disturbance in the liquor itself.

“(d.) By blowing atmospheric air, or, preferably, ozonised air produced by electric discharges, from bellows, fans, or air-pumps into the liquor. The temperature of the air blown in may be advantageously raised to that of the vat. The other operations are conducted in a similar manner to those described under the ordinary process of indigo manufacture.”

II. *The Boiling-water Process.*—Small shallow vats (2 ft. 6 in. deep) are used for this process. Water is run in and heated to the boiling-point, and the indigo plant, in small loose bundles, introduced for a few minutes only. As soon as the scalding is complete, which is known by the liquor attaining a yellowish-green colour, the solution is rapidly drawn off into the beating vat. The requisite quantity of ammonia is then added, and the liquor treated in the same manner as in the “cold water” process.

In either case, other alkalis may be used in place of ammonia, although the latter is much preferred by the patentee. He finds that ammonia has the property of combining more readily with indican and its derivatives than any other alkali. Ammonia also yields the best quality of indigo.

The chemistry of the “ammonia” process is rather obscure. Ammonia is stated to unite with the indican, forming a body which is highly susceptible of oxidation, and which yields a far greater quantity of indigo than indican itself. In the ordinary steeping vat ammonia is produced by the fermentation of the nitrogenous substances present in the indigo plant, but not in sufficient quantity to combine with, and convert the whole of the indican into the readily oxidisable body which afterwards yields indigo-blue. In the ordinary process of manufacture, therefore, there is always a great loss from a portion of the indican escaping conversion into indigo-blue. The ammonia added, as previously described, effects the complete oxidation and decomposition of the indican, thus utilising the whole of the indigo-producing bodies present in the plant.

The changes which occur during the fermentation of the *Indigofera* and during the ordinary treatment which the liquid receives in the beating vats, have never been scientifically examined, but, reasoning by analogy, principally from Schunck's investigations upon the colouring principles of the *Isatis tinctoria* or common woad, it is generally considered that during the steeping process the indican dissolves as a glucoside, and in consequence of the fermentation which ensues is decomposed into indigotin, and a peculiar sugar named indiglucin.

The indigotin would then be precipitated, but since ammonia is produced at the same time, it is, by the simultaneous action of the alkali and sugar or other organic matters present in the liquor, reduced and kept in solution, thus forming a true indigo-vat, from which the indigo is afterwards precipitated by the action of atmospheric oxygen during the beating process. However, if this simple view of the chemical changes which take place be correct, it is difficult to conceive how the addition of ammonia to the *beating vat* can affect the ultimate yield of indigo. And yet when the two methods are worked side by side with the same quality of plant, and under similar conditions, the "ammonia process" is said to yield an increase of indigo, ranging from 50 to 100 per cent. (or even more) above the ordinary system.

Indigo made by the "ammonia" process usually contains a much larger proportion of indirubin than that made in the ordinary way.* Several samples of West African indigo† have also been shown to be unusually rich in indirubin or indigo-red.

Indigotin, $C_{16}H_{10}N_2O_2$, is by far the most important constituent of indigo, as it is the one on which the value of indigo as a dyestuff chiefly depends.

Pure indigotin may be prepared in a variety of ways. A simple method consists in gently heating a little powdered commercial indigo in a platinum dish or tray covered with another dish of the same size. The indigotin sublimes and condenses on the surface of the upper dish in beautiful needles of a purple colour. It may also be obtained by boiling finely-powdered indigo with aniline, filtering whilst still hot and allowing the liquid to cool, when indigotin crystallises out. After washing with alcohol the product is pure indigotin.

Another method which gives very good results is known as Fritzsche's process, and may be performed in the following manner:—5 grammes of very finely-powdered indigo, 10 grammes of pure grape sugar, 50 c.c. of a 40 per cent. solution of caustic soda, 150 c.c. of water, and 300 c.c. of 90 per cent. alcohol, are put into a flask fitted with a cork and syphon tube. The mixture is heated on a water bath for half an hour and the insoluble matters are allowed to subside. The clear liquid is syphoned off, and a current of carbon dioxide

* Rawson, *Journ. Soc. Dyers and Col.*, 1886, p. 141.

† Rawson and Knecht, *Journ. Soc. Dyers and Col.*, 1883, p. 66.

passed through it, and then a current of air. Indigotin is thereby precipitated ; it is collected on a filter, washed (1) with dilute hydrochloric acid, (2) with water, and then dried.

Pure indigotin crystallises in beautiful dark blue or purple needles, which exhibit a coppery reflex. The powder, which is of a deep blue colour, assumes a bright red bronzy appearance when burnished. Indigo begins to sublime, according to Schunck, at 170°C . ; but other authorities give a much higher subliming point. The vapour possesses a beautiful red-violet colour, resembling that of iodine. In the open air, although the greater portion of the indigotin sublimes, it is partially decomposed, leaving a mass of porous carbon. In an inert gas it is said to volatilise without decomposition. When submitted to dry distillation, that is, heated in a closed vessel, either alone or with an alkali, indigotin is decomposed, the chief product being aniline.

Indigotin is a neutral body and is insoluble in water, ether, dilute acids, and alkalies. It is slightly soluble in boiling alcohol with a blue colour, but is again deposited on cooling. Amylic alcohol, carbolic acid, chloroform, and carbon bisulphide, also dissolve small quantities when hot, but the best solvents for indigotin are glacial acetic acid, nitro-benzene, and aniline. Boiling paraffin dissolves indigotin with a magenta colour. Concentrated sulphuric acid completely dissolves indigotin, but, since its composition is changed, sulphuric acid cannot be considered a solvent for indigotin as such. Glacial acetic acid containing a few drops of sulphuric acid, dissolves indigotin with a deep-blue colour, and on dilution with water reprecipitates it unaltered.

By the action of oxidising agents, such as dilute nitric acid, chromic acid, &c., indigotin is converted into *isatin* or indigotic acid. If nitric acid is used hot, it forms nitro-salicylic acid or picric acid, according to the strength of the acid. At the same time, other products, such as carbonic acid and oxalic acid, are formed.

Reduced Indigo.—By the action of certain bodies, termed “reducing agents” (compounds capable of giving up nascent hydrogen or assimilating oxygen), indigotin is converted into a colourless compound known as *indigo-white* or *reduced indigo*. This body is soluble in alkaline liquids, such as lime, potash, or soda. It is in this form that indigo is used for dyeing. The material to be dyed is immersed in a vat containing reduced indigo ; this, on exposure to the air, is oxidised to indigotin, which is thus fixed in the insoluble form on the fibre.

There are numerous substances which have the power in alkaline solution of reducing indigo-blue to indigo-white—*e.g.*, sodium amalgam, zinc, tin, aluminium, magnesium, &c. ; ferrous hydrate ; hyposulphurous and hypophosphorous acids ; sulphide of arsenic, &c. ; glucose, gallic acid, &c. ; and certain organic ferments. Reduced indigo is a greyish

white amorphous powder, insoluble in water and dilute acids but soluble in alcohol and ether, and in alkaline solutions; the powder on exposure to air oxidises to blue indigotin; the change rapidly takes place in the presence of water. An alkaline solution of reduced indigo has a brownish-yellow colour; an excess of reducing agent gives a clear bright yellow solution. On exposure to the air it becomes at first green, then blue, and is covered with a bronzy scum, which consists of minute crystals of indigotin. If an oxidising agent, such as potassium bichromate, be added to the solution, the blue colour of indigotin is at once developed. An alkaline solution of reduced indigo gives bulky white precipitates with salts of alumina, zinc, magnesia, and the proto-salts of iron, lead, and tin. The tin compound was formerly used in calico-printing. Reduced indigo forms two compounds with lime, one of which is soluble and the other insoluble.

Indigotin Sulphonic Acids.—It has been already stated that indigotin dissolves in concentrated sulphuric acid, thereby undergoing a change in its composition. According to the conditions either mono- or disulphonic acid is formed.

Indigotin monosulphonic acid, also known as sulphopurpuric acid and indigo-purpuric acid, is obtained by mixing 1 part of indigotin with 4 parts of concentrated sulphuric acid, and allowing the mixture to stand not more than half an hour, when it is diluted with water. A beautiful purple precipitate is formed which is only sparingly soluble in water. The sodium salt is used in dyeing under the names of indigo-purple, red extract of indigo, and red indigo-carmin.

Indigotin disulphonic acid, also known as sulphindigotic acid, is obtained by treating indigotin with a larger proportion of sulphuric acid and allowing it to act for a longer time, or by heating the mixture, or both combined. One part of indigotin treated with 10 or 12 parts of concentrated sulphuric acid at a temperature of 90° C. is converted into sulphindigotic acid in about half an hour. At the ordinary temperature it is necessary to allow the mixture to stand for 10 or 12 hours; and if the acid be not of the full strength (1·845 sp. gr.) several days are required. On diluting with water the sulphonic acid remains in solution, being soluble in about 60 parts of water. If any sulphopurpuric acid is present, it is precipitated in the form of a purple powder. The pure sulphonic acid may be obtained by adding a saturated solution of common salt which produces a precipitate of sodium sulphindigotate. The precipitate is collected on a filter and washed with a saturated solution of salt in order to remove free acid. The paste is then dissolved in water and the solution precipitated by lead acetate. The insoluble lead salt is washed and decomposed by sulphuretted hydrogen. The solution freed from lead sulphide, yields on evaporation pure sulphindigotic acid. It is insoluble in alcohol.

Sulphindigotic acid, or indigo sulphate, as it is often termed, is decolorised by reducing agents in a similar manner to indigotin

itself. The colourless solution becomes blue again on exposure to air. By the action of oxidising agents, such as potassium bichromate, and potassium permanganate, it is converted into sulphisatic acid. Both these series of reactions are utilised for the estimation of indigotin in commercial indigo.

Sulphindigotic acid is decomposed by strong solutions of caustic alkalies, forming at first a green and ultimately an orange-coloured solution. Weak solutions and alkaline carbonates form sulphindigotates, which are soluble in water, but very sparingly soluble in strong saline solutions.

The potassium salt dissolves in about 150 parts of water, and the sodium salt is somewhat more soluble. The lead salt is insoluble, and the barium salt is only very sparingly soluble.

Strong ammonia added to a solution of sodium sulphindigotate produces a green colour, which is named by V. H. Soxhlet,* indigo-green. The product has not been thoroughly investigated. It may be simply a mixture of sulphindigotate and some yellow decomposition product.

Indigodisulphonic acid may be prepared synthetically by the action of fuming sulphuric acid on phenylglycocine.†

Indirubin, or *indigo-red*, possesses the same empirical formula as indigotin, viz., $C_{16}H_{10}N_2O_2$. It is usually present in commercial indigo to the extent of 1 to 3 per cent., although occasional samples contain 6 to 8 per cent. It has been previously stated that when indican, the glucoside existing in woad, and probably in the *Indigoferre*, is submitted to fermentation or treated with dilute acids, it splits up into indigotin and sugar. This indican is very susceptible of alteration, and its modifications yield, according to existing conditions, either indirubin or indiretin and indihumin, the latter two bodies forming indigo-brown. Schunck found that when indican was mixed with caustic soda and allowed to stand for some days, the solution yielded indirubin, but no indigotin. Indican thus modified by the action of caustic soda was named by Schunck *indicanin*.

Indirubin is said to be formed in larger quantities than usual when indican is decomposed by oxalic or tartaric acid. It may be obtained from commercial indigo by extraction with alcohol or ether, indigotin being insoluble. The indigo should, in the first case, be boiled with dilute hydrochloric acid, and washed with water. A hot concentrated solution of indirubin in alcohol deposits the indirubin on cooling in the form of microscopic bundles of dark purple-coloured needles. Indirubin sublimes at a lower temperature than indigotin, and condenses again in the form of beautiful crimson needles. It is unaffected by weak acids and alkalies, but, like indigotin, is reduced to a colourless compound soluble in alkalies by the action of substances yielding

* *Chem. News*, 64, p. 85.

† Heymann, *Journ. Soc. Chem. Industry*, 1891, p. 827.

nascent hydrogen. Wool or cotton immersed in such a solution and then exposed to the air becomes dyed a fast purple colour. Indirubin dissolves in concentrated sulphuric acid, forming a deep crimson solution, which produces no precipitate on dilution with water. This solution is oxidised but slowly by potassium permanganate or bichromate. If solutions of indigotin- and indirubin-sulphonic acids be mixed together and titrated in the cold with potassium permanganate the whole of the blue compound is decomposed (decolorised) before the red is affected. On slowly continuing the addition of potassium permanganate the colour of the solution passes from a crimson to bright scarlet, and then through various shades of orange to a bright yellow.

Indirubin itself is unaffected when boiled with a mixture of potassium bichromate and sulphuric acid, whereas indigotin is decomposed.

Indirubin dyes wool and cotton crimson shades which are exceedingly fast to light. The sulphonic acid of indirubin is far faster than the corresponding indigotin compound.

When dyed on wool indirubin gives the following reactions :—

Reagent.	Indirubin-Sulphonic Acid.	Indirubin, Dyed in the "Vat."
Hydrochloric acid—conc. (cold).	No action.	No action.
Sulphuric acid—conc. (cold).	Fibre redder.	Solution crimson.
Nitric acid—conc. (cold).	Fibre yellow.	Liquid and fibre at first crimson, slowly turning yellow.
Sodium hydrate—10 per cent. (cold).	Decolorised.	No action.
Ammonium hydrate—sp. gr. '880 (cold).	Little action.	No action.
Sodium carbonate—1 per cent. (boiling).	Colour extracted.	No action.
Soap solution—1 per cent. (boiling).	Little action.	Little action.
Alcohol (boiling).	No action.	Colour extracted; solution deposits microscopic needles.

Indigo-brown.—The brown substances present in indigo are named by Schunck *indiretin* and *indihumin*. When a solution of indican is heated for some time and then treated with an acid, it yields neither indigotin nor indirubin, but a dark brown precipitate consisting of these two bodies, which are invariably present to a greater or less extent in commercial indigo.

Application of Indigo.—Indigo is a substantive dye, and consequently requires no mordant. It is used very largely both in wool and cotton dyeing. On an average some 40,000 chests, each weighing about 2 cwts., are annually shipped from India to London alone. In addition to the dyeing and printing of blues, indigo is used to a very great extent as a bottom for compound shades. Such shades, browns, olives, blacks, &c., which contain indigo are said to be *woaded*. In most cases the cloth or other material is dyed with indigo first and then filled up (mordanted, if necessary) with the other colouring matters. In any case, the indigo requires a special vat. As previously stated indigo is applied to the textile fibres in the form of indigo-white or "reduced indigo" soluble in alkalis. Many of the substances, already mentioned as being capable of transforming indigo-blue into indigo-white, are utilised on the large scale for the dyeing of indigo. For the dyeing of wool the vats are usually heated to a temperature of about 50° C. Cotton and other vegetable fibres are generally dyed cold.

The following are the most important indigo vats :—

Woad Vat.	}	used in wool dyeing.
Soda or German Vat.		
Potash Vat.		
Urine Vat.		
Hyposulphite or "Hydrosulphite" Vat.	}	used in cotton dyeing.
Copperas Vat.		
Zinc Vat.		

Dyeing of Cotton.—The principal vats for cotton are the "hydrosulphite," the copperas, and the zinc vat.

The hydrosulphite vat is prepared in exactly the same manner as described (on p. 335) for wool; the only difference being that it is usual to dye cotton in the cold. This vat is now being used to a very great extent in cotton dyeing, and is gradually replacing the old copperas vat.

Copperas or Ferrous Sulphate Vat.—This vat, which constitutes, perhaps, the oldest method of indigo dyeing, is made up with copperas, lime, and indigo. The lime decomposes the ferrous sulphate, forming calcium sulphate and ferrous hydrate, and the latter, having a great tendency to absorb oxygen and pass into ferric hydrate, decomposes water, liberating hydrogen. The hydrogen is not given off as gas, but immediately combines with the indigotin to form white indigo, which dissolves in the excess of lime present. The amounts of indigo, lime, and copperas, vary according to the work to be done, and the

order in which the ingredients are added varies with different dyers. The most usual custom is to put the indigo and copperas into the vat first and add the milk of lime gradually.

The following figures give a general idea of the proportions of ingredients used :—

Water,	1,000 gallons.
Indigo,	30 lbs.
Copperas (ferrous sulphate),	80 lbs.
Slaked lime,	60 to 100 lbs.

The indigo must be in an exceedingly fine state of division. It is ground for some days with water into a smooth thin paste.

The ferrous sulphate should be free from copper sulphate, ferric sulphate, and aluminium sulphate. Copper sulphate is injurious on account of its oxidising action, and the other sulphates are simply so much waste material. Ferric sulphate is indicated by the rusty appearance of the copperas.

The liquor before dyeing should be clear and of a brownish-amber colour. Before entering the goods, the flurry is removed by means of an iron scoop called a *skimmer*. The sediment in a copperas vat may contain a considerable amount of indigo in combination with ferrous oxide in the form of a bulky green precipitate. This should, on letting off the vat, be treated in a separate vessel with hydrochloric acid in order to recover the indigotin.

The *zinc vat* is used to a considerable extent both in England and on the continent. It is a simple vat, and possesses one or two advantages over the copperas vat. It contains but little sediment, and the constituents form no insoluble compound with indigo. It is made up with indigo, zinc dust, and slaked lime, which may be used in the following proportions :—

Water,	1,000 gallons.
Indigo,	30 lbs.
Zinc,	25 lbs.
Lime,	25 to 30 lbs.

The mixture is well stirred during a period of 18 to 20 hours, and then allowed to subside. Iron borings or filings are added by some dyers to this vat.

The zinc in the presence of lime decomposes water, forming zinc oxide. The liberated hydrogen then unites with indigotin to form indigo-white.

Unless care is taken, the vat is liable to be muddy and frothy, due to the liberation of hydrogen, but this only takes place when there is an excess of zinc.

Dyeing of Wool.—In England the woad vat and the “hydro-sulphite” vat are the two principal vats employed. The former is used largely in the dyeing of heavy cloth, and the latter principally for loose wool, slubbing, yarn, and lighter fabrics.

Woad Vat.—The reducing effect of the woad vat is due to the evolution of hydrogen by the butyric fermentation. The substances used in this vat are indigo, woad, bran, madder, and lime. For a vat of the usual dimensions, viz., 7 feet in diameter and 7 feet deep, the following figures give an idea of the quantities required for setting the vat—the smaller quantities being generally used on the Continent:—

10 to 25 lbs.	of indigo,	in fine paste.	
1½ to 5 cwts.	.	.	woad.
20 lbs.	.	.	bran or flour.
5 to 20 lbs.	.	.	madder.
24 lbs.	.	.	slaked lime.

The vat is partly filled with water, the woad added in small pieces, and the temperature raised to 60° or 70° C. The vat is well stirred, three or four times, at intervals of a quarter of an hour, and then left over night. The indigo ground in water to a perfectly smooth paste, madder, bran, and about half the requisite amount of lime are now added, and, after being well stirred, the vat is again left for a period of 20 to 24 hours. If the fermentation has proceeded satisfactorily the vat will present at this stage the following appearances:—The liquid will have a greenish or yellowish-green colour, and, on gently stirring it, blue streaks will appear, with a coppery scum or “flurry.” The sediment will be found to be in a state of fermentation, and will possess a somewhat sour but agreeable odour. If a piece of wool be immersed in the vat and exposed to the air it will be dyed blue. If these conditions are fulfilled the remaining half of the lime is added to the vat in 4 or 5 portions every 3 or 4 hours, and the temperature maintained at 50° to 60°. Generally speaking, the vat will be ready for dyeing on the third morning, although it may be “got up” in a shorter time. If the vat does not show signs of fermentation on the second morning, the lime must not be added, otherwise the fermentation will be stopped. On the other hand, the addition of lime must not be put off too long, or the putrid fermentation will set in, resulting in the destruction of the indigo. The greatest care is required in adjusting the amount of lime necessary, and the time when it should be added. A correct knowledge can only be gained by practical experience. It may be stated, however, that if the vat is fermenting too rapidly, it may be reduced by the addition of lime; and if too slowly, the fermentation may be increased by addition of bran.

Dyeing.—When the insoluble matters have subsided, an iron hoop covered with a 4-inch-mesh net (trammel net) is lowered to a depth of about a yard, and the goods dyed in the clear liquor. Pieces are stitched together in an endless band and worked under the surface of the liquor by means of a “hawking machine.” This machine simply consists of a pair of movable squeezing rollers covered with India-rubber. The old method of working piece goods is to “hawk” them by hand with two iron hooks in full width across the vat backwards

and forwards. The goods are worked in the vat for a period of twenty minutes to two hours, according to the condition of the vat and the shade required. For dark shades the goods are worked in a strong vat until the shade is rather lighter than that ultimately required, and then taken out, well wrung, and exposed to the air, in order that the reduced indigo may become oxidised and pass into the insoluble state. If the material is not well wrung out much loosely adhering indigotin is lost in the subsequent washing, and the colour will always rub. When the goods come out of the vat, they should be exposed to the air without delay, otherwise the colour may appear dull and grey. The pieces are then dyed up to shade in a weaker vat. For light blues, such as those usually given for woaded blacks, a single working in a moderately weak vat for about half an hour is sufficient. For pure indigo-blues, however, in order to obtain even and fast shades, the goods should be dyed in two or three stages, with exposure to air after each. Before dyeing it is important that the material be boiled with water and squeezed in order that the dye may penetrate and work regularly. Before dyeing with indigo, cloth is often dyed red by boiling in a bath containing camwood, barwood, or cudbear. This gives the blue a special "bloom," and also economises indigo. This "bottoming" with camwood, cudbear, &c., is especially necessary for cloth made from shoddy, which, having a grey colour, would dye a very dull shade with indigo only.

At the end of a day's working, from 7 to 20 lbs. of indigo, with the requisite amount of bran and lime, are added, and the vat well raked up, the temperature being maintained at about 50° to 60°. The vat is then covered, and next morning will again be ready for use. A vat may be used for a period of from three to nine months, when the sediment becomes so bulky that it is difficult to get sufficient clear liquor space for the dyeing operation. No further addition of indigo is then made, but as it will still contain a considerable amount of colouring matter, it is used for dyeing light shades as long as it yields sufficient colour to repay the time. Some dyers convert their old woad vats into "hyposulphite" vats, by which means the indigo is more easily "worked out."

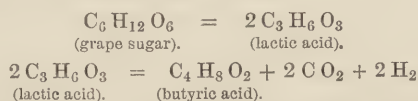
Loose wool and slubbing require a much greater amount of indigo to produce the same depth of shade than yarn or piece goods; each individual fibre being more completely dyed in the interior. Goods which are dyed in the piece only are liable to wear greyish, notably at the seams; the surface of the fibre being rubbed away and the interior dyed a lighter shade, becoming exposed. Goods which have been well "dyed in the wool" do not show this defect. Sometimes, in order to economise indigo and to produce a cloth possessing a greater resistance to wear and tear, the loose wool or slubbing is dyed a medium shade of blue, and after being woven the cloth is milled and dyed up to shade.

The washing after dyeing with indigo is of the greatest importance. Piece goods which have not been thoroughly washed will smear off or rub greatly. The pieces are first run for some time on the "dolly" with cold water, and then washed twice for about 20 minutes each time with Fuller's earth, again with water, and then with a weak tepid solution of soda, and finally with cold water. These operations are, of course, subject to slight variation. A good washing requires about five hours. The washing should not be delayed too long, otherwise the lime is liable to be so fixed in the fibre as not to be easily removed, and the colour becomes deteriorated.

The *Soda or German Vat* is used extensively on the continent, but rarely, if at all, in England. It is a fermentation vat; the ingredients used besides indigo being bran, treacle, sodium carbonate, and lime. Delmart gives the following quantities for the preparation of a soda vat:—

2 kilo. (4½ lbs.) Bengal indigo.	5½ kilo. (12 lbs.) madder.
24 kilo. (53 lbs.) soda crystals.	28 kilo. (60 lbs.) bran.
8 kilo. (18 lbs.) treacle.	¾ kilo. (1¾ lbs.) lime.

The sugar of the treacle and starch of the bran pass successively into grape sugar, lactic acid, and finally butyric acid. The final change is accompanied by the evolution of hydrogen, which immediately unites with the indigotin to form indigo-white.



An objection to this vat is that it contains caustic soda formed by the action of lime on sodium carbonate. Moreover, it does not yield so full colours with the same amount of indigotin as the woad vat. The shades, however, are brighter, and it is, therefore, well suited for the dyeing of light blues.

The *Potash Vat* is made up with indigo, madder, bran, potassium carbonate, and lime. It is similar to the soda vat, and, like it, is more easily managed than the woad vat, but is scarcely ever used in England. It contains in solution caustic potash.

The *Urine Vat*, which at the present day is of little importance, is made up with putrid urine, salt, madder, and indigo. The indigo-white formed dissolves in the ammonium carbonate, a constituent of putrid urine. The urine vat is still used in some parts of the West of England.

Hyposulphite, Hydrosulphite, or Schutzenberger and Laland's Vat.—In this vat the reducing agent is hyposulphurous acid. It may be obtained by the action of zinc upon sulphurous acid or sodium bisulphite.

In practice sodium bisulphite is used and the sodium hyposulphite in reducing indigotin to indigo white becomes re-converted into sulphite. The reduced indigo is usually made in separate vessels and

added to the vat as required. It is sent into the market in casks holding about 4 cwts. and containing about 2 per cent. of indigotin. This solution may be made in the following manner:—Take 20 lbs. of indigo (50 per cent.) ground to an impalpable paste or powder and boil with 20 gallons of water; add 25 lbs. of slaked lime in the form of cream. In the meantime, 70 to 80 lbs. of a solution of sodium bisulphite (1.25 sp. gr.) are mixed with 8 lbs. of zinc dust in a covered vessel, and kept cool by immersion in a larger vessel containing cold water. After half an hour to an hour the smell of sulphurous acid will have disappeared, when the mixture is poured into the vessel containing the indigo and lime. The mixture is heated for about an hour, made up to 500 lbs., and run off into casks. The solution will have a deep yellow colour, and, on exposure to air, the surface becomes covered with a peculiar deep rich bronzy scum.

In starting a new vat of the dimensions already given, the water is run in and heated to about 50° to 60° C.; 60 to 70 lbs. bisulphite of soda previously mixed with 6 lbs. of zinc dust, as already described, are added, followed by 6 lbs. of slaked lime made into a cream. The required amount of reduced indigo liquor is then added, and after well stirring and allowing a quarter to half an hour for impurities to subside, the dyeing operations may be at once commenced. Should the vat become oxidised a little bisulphite of soda previously mixed with $\frac{1}{10}$ of its weight of zinc is added, until the yellow colour is restored. From time to time it may be also necessary to add a little lime.

The experiences of woollen dyers with the “hydrosulphite” vat have been very varied. It is certainly much more easily managed than a woad vat, and is not so liable to get out of order. A much greater amount of work can be done, since it is not necessary to wait for a huge sediment to subside, as in the woad vats. The goods dyed are usually cleaner than those dyed in woad vats. There is much less indigo mechanically attached to the outside of the fibres, consequently, there is not so much loss in washing and boiling. Heavy-cloth dyers state, however, that the indigo does not penetrate into the interior of the cloth, and that more red colour is required to give a certain shade. No doubt a portion of the red colour is destroyed by the action of the powerful reducing agent present. Perhaps the greatest drawback to its general use is the fact that the wool is liable to be more or less attacked; acquiring a harsh handle, and appearing thinner and poorer in quality. This is due to an excess of hyposulphite, as well as to the presence of caustic soda in the vat; but the action, by careful management, may be reduced to a minimum.

New Indigo Vats.—In ordinary fermentation vats, it is well known in practice, that unless great care is taken a loss of indigo results. In order to avoid this loss, Collin and Benoist* employ a completely fermentescible food-material and a pure ferment. For

* *Journ. Soc. Chem. Ind.*, 1885, p. 493.

a vat of 8,000 litres, 16 kilos. of flour or starch are boiled for a few minutes in water containing 1.6 kilos. of sodium carbonate. The starch paste is transferred to the vat, and 8 kilos. of glucose, 5.38 kilos. of soda, and 1 kilo. of magnesia are added. Magnesia is better adapted for the neutralisation of the lactic, butyric, and other acids formed than lime. With this vat, the amount of alkali necessary to combine with the above-named acids and to dissolve the reduced indigo may be calculated with fair accuracy. As, however, the alkalinity of the vat at the commencement would be too high if the total amount of alkali were to be added at once, there is added upon the first day only one half of the soda required to neutralise the acids formed in addition to that required to dissolve the indigo. This is calculated to be 230 grms. of soda for 1 kilo. of indigo. Whilst the vat is being worked an addition of 2 kilos. of starch paste and 2 kilos. of glucose will suffice for 100 kilos. of wool per diem. The ferment, *Desmobacterium hydrogeniferum*, is obtained pure by the following cultivation process:—100 grms. of potato cuttings are allowed to digest for some time in 500 c.c. of water at 40° to 44° C. The liquid soon becomes peopled with micro-organisms, among which is the *Desmobacterium*. A flask is now filled with 1.5 grms. of phosphate of soda, 3 grms. of tartrate of ammonia, 5 grms. of glucose, 5 grms. of soluble starch, 3 grms. of sodium carbonate, 5 grms. of lime, and 1 litre of water. The flask is provided with a doubly bent tube, which dips into a basin containing 200 c.c. of water. The contents of the flask and basin are boiled for twenty minutes to effect sterilisation, and also to expel air, and then 50 to 60 c.c. of the liquid containing the *Desmobacterium* are introduced into the basin, the boiling being at the same time discontinued. The contents of the basin are slowly sucked into the flask, and when this has cooled down sufficiently for the hand to touch it without inconvenience, the bent tube is dipped under mercury and the whole maintained for four or five days at a temperature of 38° to 40° C. At the end of this period, the *Desmobacterium* will be in full activity, and in a pure condition; the liquid is then to be absorbed by sawdust sterilised at 150° C., in the proportion of three parts of sawdust to two of liquid. This is dried at 40° to 45° C., and preserved in well-closed bottles. Of this prepared ferment 50 grms. suffice for a vat of 12 cubic metres capacity. It is stated that a saving of 40 per cent. of indigo is thus effected.

J. Cowan * has recently introduced a dry powder containing indigo, by means of which a vat may be prepared ready for dyeing in a few minutes. The "compound" consists of the following ingredients, which are thoroughly mixed and ground to an impalpable powder:—

Commercial indigo, ground to powder,	100
Zinc powder,	100
Sugar,	40
Potassium carbonate,	20

* *Journ. Soc. Dyers and Col.*, 1890, p. 141.

In preparing a vat, the powder is mixed with an equal weight of liquid bisulphite of soda in a small vessel. The mixture is boiled for a few minutes and poured into the vat, which is said to be ready for dyeing in about five minutes. An alternative method consists in preparing a stock vat of any desired degree of concentration, and adding the liquid to the dye vessel as required.

Indigo-indophenol Vat.—This vat, patented by Durand, Huguenin & Co., is briefly described in the *Journal of Soc. Chem. Ind.* (1889, p. 282) and the *Journal of the Soc. of Dyers and Colourists* (1889, p. 4) 1 kilo. of dry powdered indophenol is mixed with 100 litres of water, 10 kilos. of indigo paste (containing 20 per cent. of dry indigo), 10 litres of sodium bisulphite (sp. gr. 1.38), 2 kilos. of stannous chloride, and 2.5 kilos. of zinc powder. The mixture is agitated for an hour and then treated with 8 litres of caustic soda (sp. gr. 1.35). It is again agitated, and on the following day mixed with twice its volume of cold water. After vigorous agitation it is allowed to stand until clear, when the vat is ready for dyeing.

Indigo Extract.—It has been previously stated that when indigo is treated with concentrated sulphuric acid, it dissolves, forming mono- and disulphonic acids. According to the subsequent treatment which the solution receives, the products are known as *chemic, acid or sour extract, neutral or sweet extract, refined extract, indigo-carmine, soluble indigo, &c.* When a moderate proportion of acid is used and allowed to act for a short time only, indigo-mono-sulphonic acid is principally formed. This product converted into its sodium salt forms what is known as *red or purple indigo extract*. Its use is somewhat limited; the disulphonic acid compounds having a much wider application. For the manufacture of indigo extract, one part of finely-ground dry indigo is slowly mixed with from five to six parts of concentrated sulphonic acid in an earthenware vessel. The best plan is to carefully add the indigo to the sulphuric acid in small portions at a time during constant stirring with a wooden, or, preferably, porcelain stirrer. The vessel is then placed in hot water, at a temperature of 50° to 60° C., for about an hour, taking care to stir the mixture occasionally. It will often be found that after well stirring, dry little balls of powdered indigo rise to the surface. The mixture is allowed to stand covered up for a period of about twenty-four hours. The product thus obtained is known in the dye-house as *chemic* or *Saxony blue*. It was formerly used in this state much more than at present; it now usually receives a further treatment. Unless the indigo is of very fine quality, previous to dissolving in sulphuric acid, it should be broken up into small pieces or ground to a coarse powder and treated with strong hydrochloric acid. After standing about a quarter of an hour, hot water is added, and the whole thrown on to a filter, and the mass thoroughly washed with boiling water. The partially purified indigo is then dried, ground, and dissolved in sulphuric acid as above described. In order

to convert the acid solution into extract, it is diluted with water and treated with a saturated solution of common salt, which precipitates the colouring matter. After standing an hour or two, the mixture is ladled on to a filter, made of strong woollen cloth laid upon wooden frames. Between the cloth and the frame, cocoa-nut matting or straw is placed, in order to allow the liquid portion to run off more freely. By this operation a great portion of the free acid, as well as a valueless green colouring matter, is removed. The pasty mass on the filter is known as *acid indigo extract*. It is left to drain for a period of from one to ten days, according to the "strength" of extract required, and then placed into casks.

Neutral or sweet extract of indigo is obtained in one or two ways. The acid extract may be dissolved in water, reprecipitated by salt and again filtered. In order to remove the free acid completely, the process must be repeated two or three times. The free acid is also removed by neutralising the solution with sodium carbonate, adding salt and filtering as before. A purer extract is obtained (often known as *refined extract*) by filtering the acid solution of indigo, previous to adding sodium carbonate or salt. In this way a considerable amount (varying according to the quality of indigo used) of a dirty green useless colouring matter is removed. The extract may be further purified by dissolving it in water, reprecipitating with salt, and filtering.

A purer extract is obtained (*best refined extract*) by treating indigotin or refined indigo with sulphuric acid. The refined indigo for this purpose is usually prepared by means of ferrous sulphate and lime. In the first place, what is practically a strong "copperas" vat is made (p. 331). The insoluble matters are allowed to subside and the clear liquid made to travel in shallow troughs a considerable distance, in order to reoxidise the indigotin. The liquid containing indigotin in suspension is then passed through a filter press, and the paste thus obtained dried and ground.

Soluble indigo (indigo-carminé) is the best refined extract (neutralised) made from refined indigo, dried and ground. It should dissolve in water without leaving any residue, and should be free from any green impurities.

Dyeing.—Indigo extract is not applicable to cotton, but is largely used for silk and wool, although it has been to a considerable extent, in many cases, replaced by various kinds of aniline blues. The more acid varieties are employed for dyeing wool, woollen and worsted goods. Neutral extract is employed for silk, and particularly for dyeing the worsted of mixed or union goods. It is also used in printing woollen material and worsted yarn for tapestry carpets, &c. Indigo extract is usually dyed in a bath containing sulphuric acid and sodium sulphate. If the extract is very acid, no further addition is necessary, although within certain limits the more acid the bath is,

the better is it exhausted. Sodium sulphate is employed in order to obtain more regular dyeing, the colour working on the wool or silk more slowly. In place of sulphuric acid, alum and tartar are frequently employed.

The shades produced with indigo extract are much brighter than those given by *vat indigo*, but, unfortunately, they are not fast. By conversion into its sulphonic acid derivative, the properties of indigo are entirely changed. Washing with soap and weak alkaline solutions more or less readily removes the colouring matter from the fibre, and, on exposure to light, the shade in a short time (varying of course according to its depth, and the conditions under which it is exposed) fades. Indigo extract, however, is quite as fast to light as the great majority of its numerous substitutes.

Detection of Indigo and Indigo Extract on the Fibre.—*Vat indigo* may be found on all fibres, though very seldom on silk. Extract of indigo will not be found on cotton. Indigo being a substantive dye requires no mordant. Consequently, a pure indigo-dyed cloth should contain no mordant. The presence of chromium oxide in the ash of woollen cloth indicates (but does not prove) the presence of logwood or some other mordant dye. A fabric dyed with *pure* indigo is not affected by hydrochloric acid, dilute sulphuric acid, soap, alkalies, or cold alcohol. Boiling alcohol extracts a blue colour (very little); but on cooling the small quantity of indigo separates and the liquid becomes colourless. Hot solutions of aniline, amyl alcohol, chloroform, nitro-benzene (especially aniline) extract the colouring matter to a greater extent. When the fibre is treated with cold concentrated sulphuric acid, the liquid at first becomes yellow, quickly olive, and slowly changes from green to a deep blue. On the addition of water the solution remains blue; the fibre (if wool) also is usually of a light blue colour. If the solution is boiled with a piece of white wool, the latter is dyed a bright blue shade similar to indigo extract and gives all the reactions of indigo extract. A drop of strong nitric acid gives a yellow spot surrounded by a green ring with indigo-dyed goods. This test is commonly applied by merchants and others to ascertain whether a sample of cloth is dyed with pure indigo or not. The test known as the “nitric acid test” applied alone is of no value whatever, since many other blue colouring matters give practically the same reaction. Others who have discarded the “nitric acid test” apply another, which, however, as a universal test, is also fallacious. They immerse the cloth in hot dilute hydrochloric or sulphuric acid, and if it remains blue conclude that it is indigo. As a test to distinguish between indigo and logwood it is quite satisfactory, but a great number of blue colouring matters resist the action of moderately strong acids remarkably well.

Fabrics (especially cotton goods) dyed with indigo, yield purple-coloured vapours of indigotin when gently ignited. If a piece of porcelain or glass be held over the vapours a blue deposit is obtained.

This is not a delicate test, and is of little value when only small quantities of indigo are present on the fibre. In compound shades, indigo, if present, may usually be detected by boiling two or three times with dilute hydrochloric acid, washing with water and then boiling with a weak solution (about $\frac{1}{2}$ per cent.) of sodium carbonate. The fibre is then dried and the various tests above mentioned applied. For the detection of very small quantities of indigo in compound shades (blacks, browns, &c.) Rawson makes use of a solution of sodium hyposulphite, prepared by the action of zinc on sodium bisulphite (see *Analysis of indigo*, Part XI.), in the following manner:—The material is boiled with dilute acids, and, if indigo extract is present, afterwards boiled repeatedly with a $\frac{1}{2}$ per cent. solution of sodium carbonate until the whole of it is removed. The fibre is then warmed gently with a solution of the hyposulphite and the liquid poured into a dish, or filter paper is saturated with it. In a few minutes the hyposulphite and reduced indigo (if present) oxidise, with the production of a blue colour. The blue precipitate may, if necessary, be collected and further treated. The amount of indigo present on a dyed fabric may also be determined by means of sodium hyposulphite. The process given for indigo (Part XI.) may be followed, but the precipitated indigotin cannot be weighed, since it usually contains other substances. It is dissolved in concentrated sulphuric acid diluted with water and titrated with $\frac{N}{50}$ permanganate.

In order to get a deeper as well as a brighter and redder shade on cotton yarn, after dyeing with indigo, the material is often "topped" with methyl violet or benzidine reds. Methyl violet is detected by boiling with alcohol, allowing the solution to cool, and filtering. The violet solution may be added to water and a small piece of wool dyed in the liquid. The wool is dried and the presence of methyl violet confirmed by special tests according to the tables at the end of this work. The presence of "benzidine" reds is indicated by white cotton becoming dyed red when boiled in a slightly alkaline solution with the sample of material. The dyed cotton may then be tested with acids, &c., and the results compared with the tables.

Extract of indigo is distinguished from vat indigo by the colour being removed on boiling with a dilute solution ($\frac{1}{2}$ per cent.) of sodium carbonate. On the addition of an acid to the solution, the colour is intensified, and wool or silk may be dyed blue in it. The acidulated solution is decolorised by potassium permanganate. Strong hydrochloric acid turns the fibre greenish-blue and caustic soda green. Nitric acid gives a yellow spot as with vat indigo.

In the *Journal of the Soc. of Dyers and Col.*, 1887, pp. 127, 140, 159, 178, a series of tables are given by W. Lenz, for detecting various other colours in indigo-dyed goods.

LOGWOOD.

Logwood is, perhaps, the most important of all dyestuffs. It is usually classed as a red-wood, although it is used principally for the production of blue and black shades.

The colouring principle itself is of a distinct red colour, but in combination with the more important mordants, it gives blue, violet, and black lakes.

Logwood, or Campeachy wood, is the product of a large tree of the leguminous family, known botanically as *Hæmatoxylon campechianum*, which grows abundantly in the West Indies, Mexico, and several States of South America.

The best commercial qualities are obtained from Honduras, St. Domingo, and Jamaica. The finest wood was formerly imported from Campeachy, but the supply is now almost exhausted.

Logwood was introduced into Europe by the Spaniards shortly after the discovery of America. It does not appear to have been used in England as a dyestuff until the time of Elizabeth, and then its use was only of short duration, since by an Act of Parliament it was forbidden to be used for dyeing under severe penalties on the ground that it produced fugitive colours. Large quantities of logwood were burned; and indigo suffered in a similar manner. This law was enforced for upwards of a century, but was repealed during the reign of Charles II., by which time better methods of application had been discovered.

Logwood is imported in the shape of irregular blocks or logs, weighing from three to four cwt.

The colouring matter probably exists in the form of a glucoside, and when the trees are freshly felled the wood is colourless, or nearly so. By the time the logs arrive in Europe the outside is of a dark brownish-red colour, whilst the interior is only pale yellow or light orange.

The colouring principle of logwood was first investigated by Chevreul in 1810. He found it to contain a yellowish-white crystalline body, which, on exposure to air, especially in the presence of a trace of ammonia, rapidly became highly coloured. Erdmann, in 1842, examined it further, and named the compound *hæmatoxylin*. This body on oxidation yields *hæmatein*, which is the real colouring matter in prepared logwood.

Hæmatoxylin is the result of the decomposition of a glucoside which exists in the fresh wood. Regarding the glucoside itself, little is known, except that under the influence of a species of fermentation it is decomposed with the formation of a sugar and hæmatoxylin. W. M. Gardner* considers that during the "ageing" of logwood little or no fermentation takes place, and that the process is merely one of

* *The Dyer and Calico Printer*, 1891, p. 8.

oxidation; the hæmatoxylin assumed to exist in the freshly-cut wood being slowly converted by the oxygen of the air into hæmatein. The same view is upheld by Hummel.*

In order to complete this change, the wood is either rasped or chipped, and after the addition of a certain amount of water (about 25 per cent.), placed in heaps of about 20 feet long, 10 to 12 feet broad, and 3 or 4 feet high. The heaps are frequently turned over in order to allow the air to act upon the hæmatoxylin, and also to prevent a too great elevation of temperature, which would cause excessive fermentation, resulting in the complete destruction of the colouring matter. This operation, the so-called *ageing* of logwood, simple as it may appear, requires the greatest care and skill in its management. The state of the atmosphere has a great effect upon this process of fermentation. On a warm, dull and foggy day the whole of the colouring matter in hundreds of tons of wood may be destroyed in the course of a few hours. At such periods the heaps of chipped or rasped wood in process require constant attention, otherwise excessive oxidation ensues, with the results already mentioned. When this has occurred the wood is said to be "overheated," "burnt," or "killed." Its colouring matter is not worth extracting, and if the "heating" once sets in it cannot be checked, and the whole lot is practically rendered worthless. The nature of this change is not known. It may possibly be due to the development of some micro-organism, which, in some way or other, destroys the colouring matter, in a similar manner to the destruction of indigo by excessive fermentation in a wood vat.

When the fermentation of the wood proceeds in a satisfactory manner, the hæmatoxylin is more or less completely converted into hæmatein by the oxygen of the air. The ammonia formed by decomposition of the nitrogenous matters present no doubt plays an important part in the production of the colour. In order to accelerate the operation the wood is sometimes watered with a solution of glue—a highly nitrogenous body—but the practice is attended with considerable risk of spoiling the colouring matter. Prepared or matured logwood contains from 20 to 30 per cent. more water than the original wood. During the process of "ageing," the colour of the wood changes from a yellowish-brown to a rich red-brown or dark crimson.

Hæmatoxylin, $C_{16}H_{14}O_6$, when perfectly pure, forms white prismatic crystals, but, as already stated, they quickly become coloured on exposure to the air, especially when moist, with the formation of hæmatein. Hæmatoxylin may be obtained by treating the finely-powdered wood or the extract of logwood with ether, evaporating the ethereal solution to a syrup, adding a little water and allowing it to stand for some days, when hæmatoxylin crystallises out. It is only sparingly soluble in cold water, more readily soluble in hot water; and

* Thorpe's *Dict. of Applied Chemistry*, II., p. 473.

freely soluble in ether, alcohol, and carbon bisulphide. It is non-volatile, and on being heated is decomposed. On fusing with caustic potash, pyrogallic acid is formed, which shows an intimate relation between the colouring matter of logwood and the compounds of the benzene series.

Hæmatoxylin acts as a weak acid, combining with bases to form salts which rapidly absorb oxygen from the air, being thereby converted into hæmateates. Alkalies dissolve it with a reddish-purple colour, which quickly becomes brown in the air.

Hæmatein, $C_{16}H_{12}O_6$, is produced from hæmatoxylin by the abstraction of two atoms of hydrogen, a change which takes place by the action of oxygen, especially in the presence of alkalies—



It may be conveniently prepared by exposing a solution of hæmatoxylin in ammonia to the air. The liquor assumes a dark cherry-red colour, appearing nearly black, and after some time deposits granular crystals of ammonium hæmateate, which, on addition of acetic acid, is converted into hæmatein. Like hæmatoxylin, hæmatein is only slightly soluble in cold water, but much more soluble in hot. Its solution is decolorised by sulphuretted hydrogen, although it is not reconverted into hæmatoxylin. It combines with alkalies, forming definite salts, hæmateates, which are freely soluble in water. On exposure to air, further oxidation takes place with the formation of brown insoluble bodies.

A decoction of matured logwood contains both hæmatoxylin and hæmatein, since the former is rarely entirely converted into hæmatein during the process of fermentation. The best logwood yields only about 3 per cent. of its weight to boiling water, and not more than 1 per cent. to cold water. A decoction of logwood, according to its strength, possesses an orange-yellow to a dark rich reddish-brown colour. It gives strikingly characteristic reactions with acids, bases, and various metallic salts.

Weak acids turn the solution paler.

Concentrated acids give a blood-red colouration, which becomes orange-yellow on dilution.

Potash and Soda give at first a purple colour, which becomes quickly blue and more slowly dirty violet or brown.

Carbonates of the alkalies give similar reactions, but the colour is redder, and does not become violet.

Ammonia gives a deep reddish-purple, which very quickly turns brown.

Baryta and lime water produce dark violet—nearly black—precipitates.

A solution of alum gives a beautiful rich plum colour, which develops slowly.

Normal acetate of lead gives a very dark violet precipitate.

Basic acetate of lead—bluish-black dark indigo-blue precipitate.

Ferrous sulphate—violet-black precipitate.

Ferric sulphate—similar, but redder.

Copper sulphate—dark red precipitate, which quickly becomes violet.

Stannous chloride—rich reddish-violet precipitate.

Nitrate of silver—yellowish-brown precipitate.

Bichromate of potash gives a black colouration, which develops slowly; on boiling a black precipitate is produced.

It should be observed that the colours produced in many of these reactions vary somewhat, according to the strength of the logwood decoction. In a very dilute solution, for example, lime water, instead of giving a dark violet precipitate, produces a reddish-purple colouration.

Dyeing.—Logwood is used by the dyer in various forms, according to the class of goods to be dyed, and the shade to be obtained—

1. The wood in the form of chips or raspings.
2. Logwood liquor—a decoction of the wood.
3. Logwood extract, in the form of paste or solid, obtained by evaporating the decoction.

Logwood is very extensively employed in the dyeing of all textile fibres and all classes of fabrics. Immense quantities are used for dyeing wool, cotton, and silk black, for which purpose, as a rule, the dyer prefers the chips or raspings both on the ground of being more economical and giving a tone superior to the extracts. In cotton dyeing extract is principally used. In the dyeing of loose wool, slubbing, or yarn, the usual practice is to weigh out the requisite amount of *chipped* wood into hempen bags and suspend them in the dye-vessel by means of sticks laid across, and boil for 20 minutes or half an hour. The bags are then taken out, allowed to drain, and after adding a little cold water to the vat to reduce the temperature, the material to be dyed is entered. The wood which has been thus treated is extracted a second or sometimes a third time. If, for example, it is found desirable to use 80 lbs. of wood for a certain amount of material, this might be divided into four bags and, at the same time as these bags of wood are being boiled in the vat, four more are immersed which have been once extracted and four others which have been twice extracted. After these extractions the wood is found to contain very little colouring matter and may be taken away and burnt. The woollen and worsted piece dyer uses, as a rule, rasped wood, since the fine particles are more easily removed in washing than chips. It is preferable, however, to make a decoction of the wood in a separate vessel designed for that purpose and run the clear liquid only into the dye-vat. This is now done in many dye-houses. It should be remembered, however, that a *weak* decoction of logwood deteriorates on keeping. Extracts of logwood find their chief application in the dyeing of blues and compound shades, such as greens, olives, drabs, and browns, when, comparatively speaking, only small quantities of colouring matter are required.

Logwood is an adjective dye and can therefore only be applied to the textile fibres through the medium of a mordant.

The mordant may be applied in various ways—(1) before the dyeing operation; (2) afterwards; (3) the dye and mordant may be applied together in the same bath; (4) the material may be mordanted first, then dyed, and again passed into a mordant bath. The last operation is termed “saddening” or “finishing,” and when the mordant is a *bichromate* the process is sometimes named “back chroming.”

Logwood with the more important mordants gives the following shades:—

Bichromate of potash,	. . .	Blue to black.
Salts of alumina,	Greyish violets.
„ iron,	Grey to black.
„ copper,	Dull greenish-blue.
„ tin,	Bright reddish-violet.

Dyeing of Cotton.—Logwood is most usually applied to cotton for blacks, greys, &c., through the medium of iron mordants, such as acetate or pyrolignite of iron, “nitrate of iron” (ferric sulphate), and ferrous sulphate (see p. 275). The iron oxide may be fixed direct or by means of a tannin such as sumach or myrabolans (see p. 179). The better black is obtained by tannin. For this purpose the cotton cloth or yarn, after being thoroughly wetted out, is steeped overnight in an infusion of myrabolans (about 40 per cent.); the excess of liquor is then removed by squeezing (not washing), and the cotton passed through a weak solution of lime, which causes a tannate of lime to be formed on the fibre. The material is then worked in a bath containing acetate or “nitrate” of iron or copperas at about 4° Tw. for about half an hour, again passed through weak lime water, and well washed. The tannate of iron thus formed on the fibre imparts to the cloth or yarn a deep grey colour, and, consequently, less logwood is required to produce a black than when the material is mordanted with iron salts only. Pieces are generally prepared by running through a stronger solution of tannin material in a machine known as a “jigger.” The cloth or yarn is dyed in a separate bath with 30 to 50 per cent. of logwood, and, if necessary, a small amount of fustic and usually a little copper sulphate. The dyeing is commenced cold, and the temperature of the bath slowly raised to the boiling point. In order to obtain a cleaner and faster black the cotton, after dyeing, is passed through a hot weak bath of potassium bichromate or “nitrate of iron;” and, after washing in water, scoured in soap, which takes away any rusty appearance, and thereby gives a more agreeable tone.

The following is an example of dyeing a *black* on cotton yarn. The quantities are for 60 lbs. yarn—

1. Enter in a hot solution of sumach extract (6 quarts extract (53° Tw.) in 120 gallons of water). Give three turns and allow to steep overnight.

2. Sadden in a solution of "nitrate of iron." For the first lot of yarn take $2\frac{1}{4}$ gallons of "nitrate of iron" (80° Tw.) to 180 gallons of water. For subsequent lots add $\frac{3}{4}$ gallon to the same bath.

3. Pass through lime water or a bath containing 4 lbs. of suspended chalk.

4. Dye in a bath containing logwood and fustic, using 5 lbs. of solid logwood extract and 1 lb. of fustic extract of 53° Tw.

5. Sadden in dye-bath with 1 lb. of copperas.

6. Soap at 140° F. with 4 lbs. neutral soap.

Copperas or ferrous sulphate is usually employed for inferior qualities of cotton, "nitrate" and acetate of iron for better class goods.

In the dyeing of cotton warps, and sometimes in pieces, a continuous process is employed, the warps passing in succession through the various baths.

When tannin is not used the cotton is steeped for a half to one hour in a solution of "nitrate" or acetate—preferably the former—of iron at 5° to 8° Tw. After squeezing it is worked in a bath of sodium carbonate or lime water, which precipitates ferric oxide on the fibre, and the cotton is thus dyed an iron buff. The mordanted cotton is then dyed with logwood, as in the previous case.

A common method used in piece dyeing is to pad in pyrolignite, dry, pass through lime water, and dye up in logwood.

Another method largely used for all cotton and cotton warp fabrics (linings, &c.) is to prepare with tannin, pass through copper sulphate, and dye in logwood.

There are various methods of obtaining chrome-blacks on cotton, but they are not very largely used. Perhaps the fastest is that obtained by three baths. The first bath contains a strong decoction of logwood, equal to about 500 lbs. of logwood for 100 lbs. of cotton. Of course the bath is kept for subsequent lots, a much smaller quantity being required afterwards. The cotton is boiled in this bath for about an hour, taken out and exposed to the air for some time and then worked in a cold solution of 6 to 8 per cent. of potassium bichromate and 5 per cent. of copper sulphate for three-quarters to one and a half hours. The cotton is washed and again entered into a logwood bath containing about 100 per cent. of logwood. In this bath the cotton is introduced cold and the liquid gradually raised to the boiling point. Chrome-blacks on cotton may be produced in one bath either by means of chromium acetate or by a mixture of potassium bichromate and hydrochloric acid. The dye liquors must be very strong.

A logwood-black may be also dyed on cotton in one bath by the aid of copper mordants. Copper acetate and copper carbonate are the salts usually employed. The copper carbonate is produced in the dye-bath itself by mixing sulphate of copper and soda ash in proper proportions.

A purple may be obtained on cotton with logwood by mordanting with stannous chloride. After immersing the material in a weak bath of stannous chloride, the cotton is washed in water which causes a precipitate of oxychloride of tin to form on the cloth. It is then dyed in a fresh bath of logwood decoction, entering cold, and gradually raising the temperature to the boiling point.

A logwood-blue is dyed either in a single bath or two baths by means of copper acetate or sulphate. The shade closely resembles the blue obtained by indigo, but it is not fast to light.

Direct black on cotton piece goods. (Noir réduit).

100 litres (10 galls.) logwood extract (53° Tw.)
10 kilos. (10 lbs.) bichromate of potash.
50 litres (5 galls.) acetic acid.

Dissolve the bichromate in the acetic acid and add this solution to the logwood extract, stirring for 1 hour. Add

25 kilos. (25 lbs.) chrome alum.
1½ „ (1½ lbs.) oxalic acid.
12½ litres (1¼ galls.) bisulphite of soda at 64° Tw.
25 „ (2½ galls.) pyrolignite of iron at 15° Tw.

Stir for 4 hours at 75° C.

Colour.

16 kilos. (16 lbs.) starch.
55 litres (5½ galls.) water.
40 „ (4 galls.) direct black.
15 „ (1½ galls.) acetic acid.
10 „ (1 gall.) tragacanth thickening.
1¼ „ (1 pint) oil.
2½ „ (2 pints) Persian berries extract (53° Tw.)

Boil up and allow to cool.

Add 5 litres (½ gall.) acetate of chrome (32° Tw.)
2½ „ (2 pints) bisulphite of soda.
2½ „ (2 pints) sulphoricinoleate of soda.

Pad the pieces in printing or padding machine, steam, chrome lightly, and soap. (*H. Koechlin.*)

Dyeing of Wool.—As already stated large quantities of logwood are used for dyeing wool black. Blacks are produced either by chromium mordants or iron mordants, and are distinguished as “chrome” blacks and “iron,” or more usually as “copperas” blacks.

Copperas black is the oldest style of black dyeing, and formerly was used much more than at the present time. It has been to a great extent superseded by the introduction of bichromate of potash as a mordant. A copperas black, however, if well dyed, is superior in many ways to a “chrome” black. It is less liable to turn green on exposure to light, and it is also stated that cloth dyed with “copperas” possesses a “kinder” and softer handle than cloth dyed with chrome. A copperas black may be obtained either by mordanting before dyeing

or mordanting afterwards. The latter is the more usual custom. The material is boiled for one to one and a half hours with a decoction of logwood and usually a little fustic; the amount of each varying according to the quality of the wool, texture of the fabric, and the shade desired. The quantities required may be between 40 and 100 per cent. of logwood and 5 to 12 per cent. of fustic, calculated on the weight of the material to be dyed. After dyeing, the mordanting or "saddening" may take place either in the same bath or in a separate vessel, the latter being preferred. For this operation about 5 per cent. of ferrous sulphate (copperas) and 1 to 2 per cent. of copper sulphate (blue vitriol) or copper acetate (verdigris) are added to the bath, the wool is re-entered, and boiled for three-quarters to one hour. The addition of a copper salt makes the black faster to light, and it is also considered that it assists in developing a fuller black by virtue of its oxidising action upon the hæmatoxylin. The wool must not be washed between the operation of dyeing and saddening, otherwise much colouring matter will be lost, since it is not yet fixed in the fibre but merely absorbed by it.

When the wool is mordanted previously to dyeing an addition of bitartrate of potash, in the form of tartar or argol, is made to the mordant-bath, in order to prevent the unequal precipitation of oxide of iron on the fibre. Alum and copper sulphates are usually added as well as "copperas." The wool is mordanted at or near the boiling point for one and a half hours with 5 per cent. ferrous sulphate, 1 to 2 per cent. of copper sulphate, 1 to 2 per cent. of alum, and about 10 per cent. of tartar or argol. It is taken out, squeezed, and allowed to lie in a heap for some hours, usually overnight, before dyeing. The dyeing is then proceeded with in a fresh bath, with 40 to 80 per cent. of logwood, and a little fustic, for one and a half hours at the boiling temperature. The addition of a little calcium acetate to the dye-bath increases the intensity of the colour. This addition is, however, unnecessary and superfluous in the case of waters containing a moderate amount of lime salts. Although decidedly beneficial, it is not clearly and definitely known what action takes place when the wool is allowed to lie for some time after mordanting. The simplest view to take is that the ferrous oxide in the fibre is partially oxidised to ferric oxide. Numerous modifications of these processes are adopted in particular cases. For instance, small proportions of madder, cudbear, orchil, sumach, &c., are added to the dye-bath in order to produce fuller and faster blacks.

A copperas black may be produced in a single bath on wool, but great care must be taken to have the necessary ingredients in proper proportions. A well-known black of this description is *Bonsor's patent fast direct black*, which is sent out in the form of a paste. It consists of the colouring matter of logwood in combination with oxides of iron and copper. Only small quantities of copper salts are present. The

substance is insoluble in water, but is readily brought into solution by means of oxalic acid, which changes the bluish-black liquid to amber-brown. For 100 lbs. of wool about 40 lbs. of paste are required for the first bath. After the paste has been thoroughly mixed with the liquor, 3 to 4 lbs. of oxalic acid are gradually added until the solution becomes of a dark amber-brown colour. The exact amount of oxalic acid to be added can only be determined by practice. If the bath is too acid the colour produced is thin and takes a long time to develop; but, on the other hand, if not sufficiently acid, the colour is not fast although it develops more quickly. The dyeing usually requires from one and a half to two and a half hours, at or near the boiling point; after some time a little sodium carbonate might be advantageously added in order to neutralise the acidity which increases as the dyeing proceeds. The black paste itself produces a blue black, but, if a dead black is required, all that is necessary is to add some yellow colouring matter, such as fustic. As the bath is acid, one may also use some of the many acid coal-tar colours—red, yellow, or blue—to modify the shade as required. If fastness to light and atmospheric influences is the chief thing to be aimed at, then by far the best colouring matter for the purpose is tartrazin. The bath used for dyeing the direct black is kept, since much of the colouring matter is left in solution and a smaller quantity of the black paste is required for the subsequent lots to be dyed. Oxalic acid is again added as required. A black, properly dyed in this manner, stands the action of light well.

Chrome Blacks.—Although bichromate of potash has been known as a mordant for logwood, &c., for some forty or fifty years, many dyers have still much to learn regarding its proper use. It is most important that not more than a certain amount of potassium bichromate should be used, and the effect of substances added to the mordanting bath should be carefully taken into consideration. If too much bichromate is used, the colouring matter is gradually destroyed and the dyed fabric acquires a green shade.* Chrome blacks are almost invariably obtained by first mordanting and then dyeing. In mordanting, about 3 lbs. of potassium bichromate are usually taken for 100 lbs. of wool, and the material boiled for from three-quarters to one and a half hours. For the first bath rather more potassium bichromate is required. It is not necessary that the liquor should be actually in ebullition, but it should be very near the boiling point. There is a very considerable difference in mordanting, say at 80° C. and at 95° C. After mordanting, the wool must be well washed, as it is important that all excess of potassium bichromate be removed. With slubbing and yarn the washing is done by means of a shower. Pieces of cloth are washed in a machine designed for that purpose. The material is then dyed in a fresh bath for one to one and a half hours, at the boiling temperature, with 50 to 80 per cent. of logwood

* Wilkinson on Chromium Mordants, *Journ. Soc. of Dyers and Col.*, 1886, p. 36.

and 5 to 10 per cent. of fustic. The fastness of the black to light is much increased by adding some red or violet colouring matter to the dye-bath. The substances used for this purpose are alizarin-red, gallein, galloeyanin, cudbear, orchil, camwood, &c. The best colouring matter to use is undoubtedly alizarin-red, as it is much faster than any of the other reds and works well with logwood. The bath should not be at a higher temperature than 80° C. when the wool is entered. Cudbear and orchil are often used, but the colouring matter is not fast to light. Galloeyanin, sold under the names of alizarin-violet, alizarin-purple, new fast violet, &c., is very good, and gives the black a rich bloomy appearance. Camwood, barwood, &c., are sometimes applied to the wool before chroming for the same purpose. Common blue-blacks and dark navy blues are frequently dyed after chroming in a bath containing logwood, sulphuric acid, Glaubersalt, and soluble blue or extract of indigo. The colour, however, on exposure to light soon loses its bloom, becoming grey. Blacks which have to be clean to washing require another bath after dyeing. When the goods are taken from the dye-bath they always contain some excess of colouring matter which is simply absorbed by the wool. The object of the third bath is to precipitate and fix this colouring matter in the fibre. The substance usually employed is potassium bichromate, but much less should be used than in mordanting. In this finishing or back-chroming bath the temperature of the liquor should not be higher than about 80° C., and the amount of potassium bichromate used should not exceed 1 per cent. of the weight of the wool. It is often in this finishing bath that the black is rendered liable to turn green on exposure to air by the use of too much potassium bichromate. A dyer of slubbing or yarn is frequently required to dye the material submitted to him so that it will not discolour boiling distilled water. The consequence is in many cases he uses too much potassium bichromate in the finishing bath, obtains a clean black, but one which will probably turn green on exposure to light. Rawson* has examined a great number of samples of black wool which have turned green on exposure, and in every case an excess of "chromium" was found.

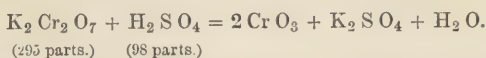
It is difficult to state a maximum amount of chrome which should be present on the fibre, since much depends upon its condition, *i.e.*, whether present as chromium oxide or as a chromate. The chromate is decidedly the more injurious. Now, when an excess of potassium bichromate is used in "back chroming" or finishing a great portion of it undoubtedly remains on the material as chromate. If too much has been used in the first chroming any chromate fixed on the fibre is, no doubt, reduced to chromic oxide at the expense of the colouring matter of the logwood. To give an approximate idea of the amount of chromium which should be present, the following case may be cited. Of two samples of yarn dyed by the same

* *Journ. Soc. of Dyers and Col.*, 1889, p. 188.

dyer under practically the same conditions, one was found to turn green in a very short time, whereas the other remained unchanged. It was found that the one which turned green contained chromium equal to 1.62 per cent. of potassium bichromate, and the other equal to 1.1 per cent.

Instead of using potassium bichromate in the third bath, one may use other salts, which, however, are generally added to the dye-bath when the dyeing has been completed. If 3 per cent. ferrous sulphate is added, and the goods worked for about a quarter of an hour longer, a dead black is obtained, and the excess of colouring matter is at the same time fixed, although the material is not as *clean* as if it had been finished with potassium bichromate. If 2 per cent. of stannous chloride is added in place of the ferrous sulphate a rich violet-black is produced. The same effect is obtained by using gallocyanin with the logwood.

In mordanting with potassium bichromate, frequently other substances, such as acids or acid salts, are added to the bath. Sulphuric acid is the most common addition; but it should never exceed one-third the amount of potassium bichromate, otherwise the shade obtained with logwood is dull. When the proportion of acid employed is as 1 to 3 of bichromate the solution practically contains chromic acid and sulphate of potash, as shown in the following equation:—



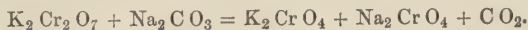
Under these conditions, a greater amount of chromium is fixed on the fibre than when potassium bichromate alone is used, but the wool is considered by many dyers to be slightly injured. Chromic acid is a very powerful oxidising agent. The addition of organic acids and organic acid salts to the "chrome" bath is decidedly advantageous, the substances usually employed being tartar (bitartrate of potash), tartaric and oxalic acids. The immediate effect of these substances is to produce the deposition of green chromic oxide in the fibre instead of chromic acid. Wool mordanted with potassium bichromate alone, or in conjunction with sulphuric acid, is of a dull yellow colour, but when organic acids are used it becomes of a pale green colour. When 3 per cent. potassium bichromate is used, from 4 to 5 per cent. of oxalic acid or tartaric acid or 8 per cent. of tartar is required to give the best results. It would be more economical to use 5 per cent. of tartar, with addition of 1 per cent. of sulphuric acid. Such large quantities of organic salts, however, are rarely used in practice on account of the expense.

The shades obtained with logwood on wool mordanted with chromic oxide are both brighter and faster than those in which the mordant was chromic acid. Probably the principal reason that tartar and tartaric acid have not been universally adopted in chroming is the

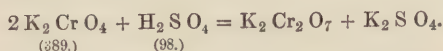
expense. It has been shown, however, that the same effect can be produced in a much cheaper way, and with superior results. The wool is mordanted as usual with potassium bichromate, with or without the addition of sulphuric acid. It is then immersed for a few minutes in a bath containing bisulphite of soda (5 per cent. on the weight of the wool), which quickly changes the yellow fibre to green. After washing, the wool is dyed as usual.

Since the chromium in chrome alum already exists in the form of chromic oxide, one might naturally expect chrome alum to give better results than potassium bichromate, but this is not the case. The colour obtained is not uniform and regular, and in order to obtain a full shade a very large amount of tartar must be used.

In the usual method of mordanting with potassium bichromate alone there is, in most cases, a considerable waste of this mordant. In an old chrome bath there is a gradual accumulation of chromate which might with advantage be utilised.* A dyer usually adds—and, for reasons about to be explained, is obliged to add—more potassium bichromate than is taken up and removed by the wool. How is this? When wool is boiled with potassium bichromate the latter is partially decomposed, chromic acid or a chromate (as well as chromic oxide) being fixed by the fibre and neutral potassium chromate remaining in the bath. If the material has been previously scoured it takes alkali into the bath which at once reduces the potassium bichromate to potassium chromate, as shown in the following equation:—



The normal chromate is a much less active mordant than potassium bichromate. One may have a very strong bath of potassium chromate without having an excess of chromium deposited on the fibre. In order to get chromium oxides equal to 1.5 per cent. of potassium bichromate deposited on the wool, the dyer may have to add each time 3 to 4 per cent. to the bath, because a considerable portion of it is converted into the less active form. A "chrome" bath which has been worked 15 or 16 times has been known to contain about 20 lbs. of chromate as such and as bichromate. It need not have contained more than 5 or 6 lbs., the quantity added for the first lot of wool. All that is necessary to prevent this accumulation and waste of chromate is to add sulphuric acid in the proportion to convert the neutral chromate into bichromate. The reaction takes place in accordance with the following equation:—



Practically, for every four parts of normal potassium chromate present in solution, one part of sulphuric acid should be added.

* Knecht, *Journ. Soc. Dyers and Col.*, 1889, p. 184.

It would well repay the dyer to make rough tests of his "chrome" baths from time to time both as regards *condition* (acidity or alkalinity as the case may be) and as regards the amount of chromate present. In order to test the condition of the bath, the best *indicator* is *lackmoid paper*. (See *Analysis*, Part XI.) If the whole of the chromium is present in the form of *bi*-chromate, the paper shows a neutral reaction; if normal chromate be present red paper is turned blue, whereas an excess of acid turns blue lackmoid paper red.

To find the amount of acid to be added, the following simple method is recommended:—Take 1 litre of the chrome liquor and pour it into a white porcelain basin. Gradually add from a burette, with constant stirring, a solution of sulphuric acid containing 6 grms. per litre until a piece of blue lackmoid paper shows a neutral reaction. The number of cubic centimetres required to produce this effect corresponds to the number of ounces of sulphuric acid (D.O.V.) to be added to 1,000 gallons of "chrome liquor."

In order to find the amount of chromate and bichromate present in a vat, the following mode of procedure is, perhaps, the simplest:—Weigh 1 gramme of granulated ferrous ammonium sulphate into a porcelain basin, add 100 cubic centimetres of a 2 per cent. solution of sulphuric acid, and run in from a burette the chrome liquor until a drop of the solution ceases to produce a blue colour when brought in contact with a drop of potassium ferricyanide. The number obtained by dividing the figure 126 by the number of cubic centimetres of "chrome" liquor required, equals the number of pounds of potassium bichromate in 100 gallons.

Direct Chrome-black.—If logwood liquor and a solution of potassium bichromate are boiled for some time a black precipitate is obtained, which may be collected and used for dyeing a *direct chrome-black*. For this purpose the paste is mixed with water in a vat, and dissolved in oxalic acid, and the wool dyed in the solution one and a half to two hours. The results, however, are not as good as those obtained by Bonsor's black, where the bases copper and iron are used.

Woaded blacks are those which contain more or less indigo. The name arises from the indigo being usually applied in what is called the "woad vat"—woad being one of the ingredients of the vat. But in whatever way the indigo is applied (except when indigo is dissolved in sulphuric acid) the goods are commercially known as *woaded*. After "woading" the material may be dyed up either by the "copperas" or "bichrome" method.

In the case of *woaded chrome-blacks*, the indigo is sometimes applied after chroming in order to prevent loss of indigo, but the usual custom is to dye with indigo before chroming. This chroming must be done without acid, otherwise much of the indigo will be oxidised and destroyed. In light shades sometimes there is scarcely any indigo left after chroming.

The object of woading or indigo-dyeing is to give a black faster to light. If a fair amount of indigo is used the colour is undoubtedly much superior; but, in many cases, the quantity of indigo put on is so little that its effect must be inappreciable. Many woaded blacks are better only in name than so-called common fast blacks. A chrome-black dyed with logwood, fustic, and alizarin-red, where the chrome has been previously reduced to chromic oxide, is far superior to a great many of the woaded blacks, where logwood and fustic have only been used in addition to a little indigo.

Logwood-blues are produced on wool much in the same way as chrome-blacks—smaller quantities of mordant and dye being used, and the addition of fustic omitted. The amount of potassium bichromate should be reduced to a minimum, and it should be in the reduced state. The lighter the shade the more quickly, of course, any change is noticeable. A purplish shade is obtained by adding a little stannous chloride (about 1 per cent.) towards the end of the dyeing operation. The same effect is obtained, and with better results as regards fastness, by adding alizarin-red, gallein, or gallo-cyanin to the dye-bath. In some cases the wool is first dyed a light shade of indigo, as in woaded blacks.

Some dyers mordant with alum and tartar for logwood-blues, using about 6 per cent. of alum or 4 per cent. of aluminium sulphate, and 6 to 8 per cent. of tartar. In such cases it is advisable to add either chalk or calcium acetate to the dye-bath unless the water already contains much lime.

Sometimes water-blue is added to the mordant-bath for brightening the ultimate colour.

Logwood-purple is obtained by mordanting with about 4 per cent. of stannous chloride and 4 to 6 per cent. of tartar, and dyeing in a fresh bath with 20 to 40 per cent. of logwood. The colour is not fast, and the same shade is easily obtained by more permanent dyes. Tin salts, furthermore, always give the wool a more or less harsh feel.

Dyeing of Silk.—Logwood is used in very large quantities for the black dyeing of silk, and it is fixed on this fibre principally on iron mordants; aluminium-, copper-, and tin-mordants are of minor, and chrome-mordants of no importance for the fixation of logwood on silk; nor is logwood used for the production of colours other than black on silk.

The black dyeing of silk is essentially different from the usual dyeing methods, since the intention is usually not only to impart a black shade to the material, but also to add to its weight; this increase may even be as much as four times the weight of the fibre itself (*i.e.*, 400 per cent.) The weighting is effected by the fixation of tannin-iron and tannin-tin lakes in the fibre, chestnut extract, gambier, pyrolignite, and "nitrate of iron," yellow prussiate of potash, and stannous chloride being the most important materials. When fixed in large quantities the tannin-iron lakes are by themselves sufficient to dye the silk fibre

black ; but for the production of fine black shades the dyeing is finished with the aid of logwood.

In various parts of this book notes are found on black dyeing of silk and these may be collected in this place.*

Black dyeing of silk may be divided into

- I. Black on Raw Silk.
- II. Black on Discharged Silk.
- III. Black on Souple Silk.
- IV. Black on Wild Silks.

I. *Blacks on Raw Silk*.—These are principally dyed on yarns which are intended to serve in pile fabrics, sateens, &c., as the basis of the fabric, and are visible on the back of the goods only. The silk is not boiled-off in order that the strength of the fibre may be preserved, and, consequently, hot soaping during the dyeing process is to be avoided. Yellow silks are sometimes bleached with aqua regia before dyeing.

Three different kinds of black on raw silk may be distinguished :—

- 1. Black with Chestnut Extract and Pyrolignite of Iron.
- 2. Black with Prussian Blue.
- 3. Black with Logwood (without heavy weighting).

The process of dyeing black on raw silk with chestnut extract and black liquor is described under the heading of *Iron mordants on silk* (p. 278). It weights up to 200 per cent.

Hummel (*Dyeing of Textile Fabrics*) describes the following heavily charged black for fancy goods :—Dye raw silk black by alternate treatments with chestnut extract and pyrolignite of iron ; after repeating these operations fifteen times the silk is weighted to about 400 per cent. Soften and brighten with 10 to 20 per cent. of olive oil, &c. In the first bath of chestnut extract the liquor is heated sufficiently to soften the silk-gum (*soupling*).

A finer black is produced by dyeing the silk blue with “nitrate of iron” and yellow prussiate of potash and topping with chestnut extract. If a heavy weighting is required the raw silk is treated about three times with “nitrate of iron” and subsequently with yellow prussiate, as described in the above-named chapter (p. 281). The silk thereby receives a charge of about 24 per cent. ; each iron bath yielding 4 per cent., or altogether 12 per cent. ; and the same amount is added by the subsequent conversion of the ferric oxide into Prussian blue. After a good washing in running water the silk is dyed black and weighted still more in a bath of chestnut extract ; 150 per cent. of extract, 15° Tw. (of the weight of the silk), are used, and the material is worked in this bath at 40° to 45° C. for some time, whereby a weighting of 30 to 40 and even 50 per cent. is added to that already produced, or 60 to 70 per cent. altogether. By repeating the whole treatment three times a weighting of more than 200 per cent. may be effected.

* M. Moyret, *Teinture des Soies*.

In cases where the material does not admit of being subjected to so many treatments a light black may be produced with logwood after the methods used for the so-called "English black" (on boiled-off silk).

Prepare a bath with—

50 to 60 per cent.	logwood,
25 to 30 ,,	fustic,
4 to 5 ,,	copperas,
1 to 2 ,,	acetate of copper,

and sufficient water (20 times the weight of the silk). Dissolve the salts in the water, add the decoctions of the dyewoods and stir well. Work the silk in this bath for half an hour, lift and heat to 60° C., and work again for half an hour. Expose the silk which has now acquired a brownish colour on rods to the open air for one hour, rinse well, and hydro-extract. The bath is run off.

Work the silk for one hour at 50° C. in a decoction of 50 per cent. of logwood; then rinse well. The bath is not preserved.

Work for one hour in a tepid soap bath, containing 30 to 50 per cent. of good soap, wring, rinse in running water and hydro-extract; this treatment softens the silk and improves the shade. Brighten with a moderate amount of acid; vegetable acids or lime juice are most suitable.

II. *Blacks on Discharged Silk*.—The discharging of silk for black dyeing, especially for heavy blacks, requires great care in order that the goods may suffer as little as possible and be able to resist the great number of operations they are subjected to.

A great many different methods of black dyeing discharged silk are known; the following are the most important processes:—

1. English Black (Light Black).
2. Blacks for Pile Goods (not weighted).
3. Lyons Black (with Prussian Blue; moderately weighted).
4. Mineral Black (moderately weighted).
5. Heavy Black (with Catechu and Tin Crystals).
6. Heavy Black (with Acetate of Lead; very heavily weighted).

1. *English Black*.—This black is principally used for tender materials which do not allow a great number of treatments or which are to be woven together with white yarns.

Dye with—

50 per cent.	logwood,
50 ,,	fustic,
5 to 6 ,,	copperas, and
2 to 3 ,,	acetate of copper,

half an hour at 50° to 60° C., lift and heat to 70° C., and work half an hour more; run the dye-liquor off and allow the yarns, which now possess a brownish colour, to hang one hour on the rods in the dye-vat; after this rinse well. Dye in a fresh bath with 50 per cent. of logwood and 50 per cent. of soap; enter at 50° to 60° C., turn half an

hour, lift and heat to 70° to 75° C. and turn another half hour. Run off the liquor and rinse first in the dye-vat and subsequently in running water; hydro-extract. Soften and brighten with 2 to 4 per cent. of oil which has been mixed with sufficient acid to give a slightly sour taste.

A fine greenish-black is thus produced without any weighting of the silk.

If an increase of the weight is required the silk may be treated once or several times with "nitrate of iron" in the manner described on p. 279 for boiled-off silk. By three treatments 12 per cent., or one-half of the loss the silk suffers by the discharging process, may be recovered; a further weighting with "nitrate of iron" would injure the material on account of the destructive influence of the ferric salt on the silk fibre. A light bath of catechu at 50° to 60° may follow, and then the silk is dyed and finished precisely as in the preceding method. The mordanting with "nitrate of iron" imparts to the goods a fuller and less greenish tone which even becomes bluish if a smaller amount of fustic is used.

2. *Blacks for Pile Goods (without weighting).*—Black velvets and plushes are desired to appear bluish-black when viewed direct or "underhand" and black-blue when viewed through or "overhand." This effect is produced by mordanting with alum and by dyeing without fustic.

Work for some time in a cold concentrated solution of alum, steep overnight, and rinse next morning in calcareous water. Dye as for "English Black," first with 50 per cent. of logwood, 3 to 4 per cent. of acetate of copper, and a little copperas, and subsequently in a soap bath with logwood; less copperas than for "English Black," and no fustic is used. No scroop being desired for pile goods, the yarns are turned a few times in a weak tepid bath of neutral soap for softening, hydro-extracted, and dried without rinsing. Lustreing of the yarns in the moist state is avoided, since it deepens the colour too much. The material is sometimes dyed with methyl-violet or aniline-blue before the mordanting, to produce a finer bluish tone; great care is necessary that the dyestuff be not stripped by the subsequent treatment.

Like the English black this black does not increase the weight of the silk.

3. *Lyons Black (Black with Prussian blue, moderately weighted).*—Mordant two or three times with "nitrate of iron," soap, and dye blue with yellow prussiate of potash (p. 281). A weighting of 16 to 24 per cent. is obtained; or by a three-fold treatment with nitrate, &c., the loss sustained by the discharging is recovered and the silk brought to "pari." A further weighting of 4 per cent. may be added by one more treatment with "nitrate of iron" after the blue dyeing, and subsequent rinsing with water to precipitate the ferric hydroxide (hot soaping would affect the Prussian blue). Work the silk after these treatments one hour in an old bath of catechu (gambier) standing at

4° to 7½° Tw., the temperature of which should not exceed 50° C., so that the Prussian blue may not be decomposed and the shade become too dark; rinse and hydro-extract. The silk acquires in the catechu bath an overcharge (over pari) of 15 per cent. and becomes more greenish. For the weighting of silk pale cutch (gambier) is used, since dark cutch does not yield satisfactory results, the colours not resisting the action of soap. Experience has proved that old baths of catechu give better results as to shade and to weight than new ones; they are maintained at the same specific gravity (and strength) by regular additions of fresh solutions of catechu. To obtain a more bluish shade work in a cold concentrated bath of alum and rinse in water. Dye exactly as for English black (p. 357), first with logwood, fustic, copperas, and acetate of copper, and subsequently with logwood and soap. On account of the preceding aluming, however, great care is required to avoid uneven dyeing, and 100 per cent. of a very fatty soap (calculated on the weight of the silk) are required for the second dye-bath. Enter at 50° to 60° C., and heat very gradually to 80° to 85°; the heating may last 5 to 6 hours. After the dyeing is finished run off the liquor, rinse first in the dye-vat with soft water and then in running water. Brighten with 4 to 6 per cent. of good olive oil and lime juice, and finally lustre.

This black possesses a very fine bluish tone, and gives 5 to 15 per cent. weight above "pari."

4. *Mineral Black*.—This black gives a moderate weighting (about 30 per cent.); it is inferior to the preceding black in fineness of shade. The operations required are three or four treatments with "nitrate of iron," blue dyeing with yellow prussiate of potash, hot catechuing, dyeing with logwood and soap (as for English black, p. 357), brightening and lustreing. For catechuing, the silk is worked one hour at 70° to 75° C., in an old bath of catechu (gambier) (4° to 7½° Tw.) which is used continuously. Catechu acts at the elevated temperature on Prussian blue, and is fixed in large quantities, adding a weighting of 25 to 30 per cent. to the charge already obtained by the preceding treatments, which may be as high as 36 per cent.; hence this method produces a weighting of 50 to 60 per cent., or an overweight above "pari" of 25 to 35 per cent. After the catechuing follow the dyeing with logwood and soap, softening, brightening, and lustreing, exactly as for English black. The shade produced is a very full greenish-black.

The following black is very similar; but it possesses a better, more bluish shade, and yields about 6 per cent. more weight. It differs by the special treatment with pyrolignite of iron and the subsequent catechuing, and consists of the following series of operations: two, three, or four treatments with "nitrate of iron," blue dyeing with yellow prussiate, one more treatment with "nitrate of iron," hot catechuing, mordanting with pyrolignite of iron, tepid catechuing, dyeing with logwood and soap, brightening and lustreing. For the

tepid catechuing, after the first mordanting with pyrolignite of iron, sometimes a dyeing with logwood without soap is substituted to obtain a more bluish-black. The pyrolignite bath is used at a specific gravity of 3° to $4\frac{1}{2}^{\circ}$ Tw., and at a temperature of 20° to 30° C.; the silk is turned half an hour, rinsed, and worked half an hour in an old tepid catechu bath (7° to 8° Tw.); the pyrolignite bath and the catechu baths are used continuously. The other operations are exactly the same as for the preceding "mineral black."

5. *Heavy Black with Catechu and Tin Crystals.*—This method yields a weighting up to 80 and even 100 per cent.; it produces a good shade, but the weighting is effected at the expense of the strength of the fibre. The peculiarity of this process is the application of catechu and tin salt; the other operations resemble those which have been described in the preceding section.

Mordant 6 to 8 times with "nitrate of iron," soap, and dye blue with yellow prussiate; each mordanting yields 4 per cent. weight, and 6 or 7 treatments would give 24 to 28 per cent.; this result is doubled by the blue dyeing so as to produce a weighting of 48 to 56 per cent., or an overweight above "pari" of 24 to 30 per cent. Prepare a fresh bath of gambier (100 to 150 per cent. of the weight of the silk) in a dye-vat of suitable dimensions which admits of working 300 lbs. simultaneously, keeping, however, the hanks closely together to prevent access of air as far as possible; work the yarn half an hour at 50° C., lift, heat to 70° to 80° and add a solution of 8 to 12 per cent. tin crystals (of the weight of the material). By the addition of tin crystals the bath changes from brown to yellow and is partially precipitated; work the yarn again for 1 or 2 hours and allow to rest in the bath over night or longer. The material will not be injured by remaining in the bath for several days if it is prevented from rising to the surface. Some dyers enter the catechu solution at a higher temperature than 50° C., or even at the boil, and obtain a heavier weighting by the powerful action of the catechu on Prussian blue. After taking the yarn out of the bath rinse well in water and run off the catechu liquor; after settling, the clear liquor may be used again for this operation, whilst from the sediment tin may be recovered (see p. 291). The silk changes by the preceding treatment from blue to a dull green, and acquires a harsh feel. Soften by working 1 hour at 50° to 60° C. in a bath containing 33 or even 50 per cent. of soap, then rinse and hydro-extract whilst the soap bath is run off. Work the silk in another bath of catechu (100 per cent.) 1 hour at 70° to 75° C., rinse and hydro-extract; preserve the bath. Dye with 50 per cent. of logwood and 50 to 60 per cent. of soap, first half an hour at 50° to 60° C., and then at 70° to 75° until the desired shade is produced. By the combination of the purplish shade of the logwood-tin lake and of the above-mentioned greenish-black tone, a violet shade of black is obtained.

The weighting depends to a great extent on the mordantings with

"nitrate of iron" in the beginning of the operation; the first two mordantings allow of a weighting of altogether 45 per cent.; the following mordantings are less effective and admit only 10 to 15 per cent. increase each; thus about 110 per cent. weighting, or an over-weight of 85 per cent. above *pari* are obtained ultimately, if the silk was treated seven times with "nitrate of iron."

The reddish tone of this black may be changed to a more bluish and finer shade by a treatment with pyrolignite of iron, precisely similar to that described for mineral black (p. 359). After the second catechuing, work the silk for one half hour to one hour in a weak bath of pyrolignite of iron, rinse, hydro-extract, turn for half an hour in an old bath of catechu (4° to 7½° Tw.) at a temperature not exceeding 50° C., and after draining rinse and hydro-extract; this treatment effects also a weighting of 4 to 5 per cent. Dye as before; if the goods should become reddish, heat to 80° to 85° C., and, if necessary, add some soap; finally run off the liquor, rinse the silk first in the dye-vat and subsequently in running water, hydro-extract, and brighten with 6 to 8 per cent. of acidulated oil emulsion. The silk is ultimately finished by lustring.

A further increase of the weight may be effected by treating the silk after dyeing and washing (1) in a weak bath of catechu at 50° C., (2) steeping in pyrolignite of iron, (3) again in catechu at 50° C., and (4) dyeing with logwood and a large amount of soap; these four operations may even be repeated in the order given.

6. *Heavy Black (weighted to 350 per cent.) with acetate of lead* is described by Moyret. It is also used for fancy goods, the raw material of which is waste silk. Discharge in soap at the boil or at 60° to 70° C.; soak in 150 per cent. of chestnut extract 15° Tw., at 40° to 50° C.; rinse; work in pyrolignite of iron at 60° to 70° C.; repeat the treatments with chestnut extract and black liquor according to the desired weighting up to six times, increasing the amount of chestnut extract gradually up to 250 per cent.; six treatments yield a weighting of 250 per cent. After this pass through a bath of basic acetate of lead which has been prepared by saturating a solution of pyrolignite of lead, 8° to 15° Tw., with litharge; in this bath the silk is weighted about 100 per cent. more, extracting a corresponding amount of lead oxide from the bath.

The previously described methods for increasing the weight of the silk, such as treatment with "nitrate of iron" and yellow prussiate or with gambier and tin crystals, may also be employed to attain a higher charge.

III. *Black on Souple Silk*.—The soupling of silk for black does not precede the dyeing but forms part of the dyeing itself. Mordant the raw silk 2 to 6 times in "nitrate of iron," taking care that the bath remains sufficiently basic; the raw silk possesses a direct affinity for ferric oxide, and extracts it from the bath, leaving free acid behind,

whereas boiled-off silk absorbs the salt without dissociation; dye blue with yellow prussiate. The next operation is the soupling with a tannin, such tannins as give blue colourations with ferric salts being employed, notably tannic acid, extract of gall-nuts, myrabolans, and divi-divi. Work in a solution of the tannin (standing at 6° to 8° Tw.) at 50° C. for half an hour, lift and heat to 70° C., work again, and so on several times, raising the temperature gradually to 90° or 95°; this operation lasts from 2 to 5 hours, and finally the goods may be left in the bath over night. The tannin-bath is used continuously. Some stannous chloride (8 to 15 per cent., more or less, according to the number of mordanting treatments with "nitrate of iron") may be added to the tannin-bath on heating the first time; the same precautions as to access of air as usual are required, and the bath is finally run off. The further operations are similar to those used for the dyeing of boiled-off silk, for instance, to those described for the production of mineral black (p. 359). They consist chiefly in dyeing with logwood in a soap-bath with or without mordanting with pyrolignite of iron immediately after the soupling. In dyeing souple silk care must be taken, however, never to raise the temperature of the soap-bath above 50° C., not to dissolve the silk gum. The weighting of the silk may be increased to 80 and even 100 per cent. By repeated treatments of the soupled silk with "nitrate of iron," chestnut extract, tin crystals, and prussiate of potash, even double this amount may be reached. The weighting of souple silk is more complicated than that of raw or discharged silk, is principally a matter of experience, and cannot be well described.

IV. *Black on Wild Silks*.—The wild silks offer difficulties in dyeing generally, and still more so in black dyeing, since they do not take up colouring matters easily, and still less so iron mordants.

Moyret (*l.c.*) recommends the following process for black dyeing of tussur:—Discharge with dilute caustic soda at 60° to 80° C. Mordant once or twice in "nitrate of iron" and fix with caustic soda. Dye blue in a weak bath of yellow prussiate of potash. Work in a weak bath of chestnut extract, and pass then through pyrolignite of iron; repeat these last two operations twice (not for weighting, but for saddening the shade). Brighten with 6 to 8 per cent. of olive oil.

Detection of logwood on dyed fabrics.—The detection of logwood on dyed fabrics when other colouring matters are absent is a comparatively simple matter; but in many compound shades its presence can only be discovered by the employment of numerous delicate tests. The information generally given on this subject refers, as a rule, only to the pure colouring matters; but, in many cases, these reactions are of little help. However, in the first place, the pure colouring matter should be studied and all reactions carefully noted. The detection of the mordant which has been used often throws much light on the kind of colouring matter which may be present. If no mordant

is present on the fibre one may safely exclude all the adjective dyes, such as logwood, &c. In order to test for the inorganic mordants a portion of the fabric is ignited in a platinum or porcelain dish and the ash which remains, free from carbon, treated as follows:—

Chrome Mordants.—Ash, yellowish- or brownish-green. Add a little potassium chlorate and fuse—a bright yellow mass obtained. If dissolved in water and acetic acid and acetate of lead added a yellow precipitate is obtained, confirming the presence of chromium. If a trace of chromium is present it *may be* detected by means of a borax bead, which acquires a green colour in the presence of chromium.

Iron Mordants.—Ash, reddish-brown colour. Dissolve in hydrochloric acid, add potassium ferrocyanide; a blue precipitate indicates iron.

Copper mordants (usually found in combination with iron and sometimes with chrome).—Dissolve the ash in hydrochloric acid, add a slight excess of ammonia and filter. If much copper is present the filtrate will be blue. Smaller quantities are detected by adding acetic acid and potassium ferrocyanide, which produce a reddish-brown precipitate or colour.

Aluminium Mordants.—Ash, white. Dissolve in hydrochloric acid and add ammonia, which gives a white precipitate in presence of alumina. Confirm by heating on charcoal with cobalt nitrate; a blue mass is thus obtained.

Tin Mordants.—Ash, white; yellowish when hot. Globules of tin are obtained by heating on charcoal; small quantities detected by the red colour imparted to a borax bead containing a trace of oxide of copper when heated in the reducing flame.

A logwood-blue or -black gives the following reactions with the more common reagents:—

Reagent.	Chrome Mordant.	Iron Mordant.
Hydrochloric acid, sp. gr. } 1·16, }	red-violet (slowly).	crimson, more easily extracted.
Sulphuric acid, sp. gr. 1·84,	olive-brown, yellow on dilution.	olive-brown, yellow on dilution.
Sodium hydrate, 10 per } cent. }	slowly violet.	quickly violet.
Ammonia (strong), . . .	little action, very slowly violet.	little action, very slowly violet.
Stannous chloride, } Hydrochloric acid, } Water (equal parts), }	red-violet.	light red.

The above tests are all made in the cold, and may be conveniently performed in porcelain basins. Boiling alcohol has no effect upon a

logwood colour, neither has a boiling solution of soap nor a $\frac{1}{2}$ per cent. solution of sodium carbonate. Boiled with dilute hydrochloric or sulphuric acid (5 per cent.) the logwood is more or less removed and the solution becomes red or orange-red. The fibre is of a light purple or reddish-drab colour. On adding an excess of caustic soda to the acid solution, the latter is immediately turned to a deep violet colour, which, however, gradually disappears with the formation of a brown precipitate, while the solution also remains tinted brown. If this test is made with a logwood-black, -blue, or -violet, which contains alizarin, the alkaline solution remains purple or violet after the logwood has been precipitated. On now adding a dilute acid the purple or violet colour, if due to alizarin, will turn to a light yellow. Dark fast navy-blues on wool are frequently dyed either with indigo, alizarin-blue, or gallocyanin, and logwood is often used in conjunction with them, being very much cheaper. In some cases this is permissible, but in others, customers object to the use of logwood altogether in such shades. Consequently, the detection of logwood in the presence of these colouring matters is a matter of some importance. With indigo its detection is easy; but the presence of a small amount of logwood with alizarin-blue and gallocyanin cannot be so readily ascertained. The following method can be recommended. It is exceedingly simple, but requires close observation. It depends on the action of cold concentrated sulphuric acid. This reagent gives with logwood, as already stated, a brownish-red solution, which becomes yellow on dilution with water. It gives, with alizarin-blue, a deep violet-blue liquid, which becomes red-violet on dilution; with gallocyanin, a violet liquid, which becomes redder on dilution; and with indigo, at first green, then deep blue, which remains blue on dilution. The colour of the diluted solution is more clearly seen after filtering. The yellow colour of the logwood is more intense than the other solutions, and a very small amount is sufficient to modify their shade. The delicate pink given by gallocyanin and alizarin-blue becomes red, orange-red, orange to orange-yellow, according to the amount of logwood present. In a mixture of indigo and logwood, the colour of the liquid is green after adding sulphuric acid and diluting with water, but on passing the solution two or three times through a filter the indigo is retained and the logwood only is obtained in the filtrate. This reaction is of importance, since it enables one to distinguish between logwood, gallocyanin, and alizarin-blue in the presence of indigo; which, otherwise, would be a very difficult problem. Logwood is at once detected in an indigo-dyed fabric by boiling with a 5 per cent. solution of sulphuric acid, which removes the logwood, as previously stated. Gallocyanin, if present, would also be partially removed. After repeating the operation once or twice, the colour remaining shows approximately the depth of indigo present in such a mixture, but, if the wool contains chromium in the form of a chromate, a portion of the indigo will have been destroyed

by the chromic acid liberated during the reaction. It should also be remembered in applying this test that several blue colouring matters besides indigo are unaffected, or only slightly affected, by boiling acids. Cloth dyed with indigo and logwood colours hydrochloric acid *red*, and a 10 per cent. solution of caustic soda *violet*; whereas pure indigo gives up no colour to either liquid. The ash of wool or cotton fabrics dyed with logwood and indigo will contain either chromium or iron, or both; whereas pure indigo will contain neither, or, at most, a trace of iron.

F U S T I C.

This dyestuff is known as old fustic, Cuba wood, and yellow wood. It is the wood of a tree belonging to the natural order *Urticaceæ*, known botanically as *Morus tinctoria* or *Maclura tinctoria*. It is a native of Brazil, Mexico, and several of the West Indian Islands, the best qualities being produced in Cuba and Tampico.

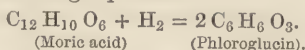
According to most authorities, fustic contains two colouring matters, which were first isolated by Chevreul. One is readily soluble in water, which Chevreul named *morin jaune*, and the other, which is nearly insoluble, he called *morin blanc*. These two colouring matters have been investigated by Hlasiwetz and Pfandler, as also by Wagner and Löwe. If a concentrated syrupy aqueous decoction of fustic is allowed to remain at rest for some days, an abundant crystalline deposit is formed. Commercial fustic extract will answer the purpose. The crystalline deposit is washed rapidly with a little cold water and strongly pressed. The product is then boiled twice with water, which yields a solution containing morintannic acid (the *morin jaune* of Chevreul), and a residue of moric acid (*morin blanc*), and morate of lime. The aqueous solution is concentrated by evaporation, and the morintannic acid precipitated by the addition of a little hydrochloric acid. The product is recrystallised two or three times from an aqueous solution acidulated with hydrochloric acid. In order to isolate pure moric acid the residue, which is insoluble, or nearly insoluble, in water, is treated with dilute hydrochloric acid (to decompose the calcium morate), and dissolved in alcohol. On the addition of two-thirds of its bulk of water the solution deposits moric acid in the form of yellow needles, which may be further purified by repeated crystallisation from weak alcohol.

Morintannic acid, which is also known as *Maclurin*, is deposited from its solution in the form of a light yellow crystalline powder composed of microscopic needles. It is soluble in 64 parts of cold, and 2.14 parts of boiling water, and is also readily soluble in alcohol, wood spirit, and ether. The ethereal solution is greenish by reflected, and brown by transmitted light. It melts at 200° C., gives off water and acid vapours at 250°, and completely decomposes at 270°. The composition of morintannic acid is $C_{13}H_{10}O_6$. When heated with a strong solution of caustic alkali it yields phloroglucin and protocatechuic acid. Morin-

tannic acid dissolves in cold concentrated sulphuric acid with a yellow colour, and is reprecipitated on the addition of water. The strong acid solution, if allowed to remain at rest for some days, deposits brick-red crystals of rufimoric acid. A solution of morintannic acid, treated with zinc and sulphuric acid, assumes at first a red colour which turns slowly to orange. The solution then contains phloroglucin and machromin. Machromin crystallises in slender needles, which become blue on exposure to the air. Hydrochloric acid gives a blue precipitate and the alkaline solution also becomes blue on exposure to the air. Ferric chloride added to a solution of machromin produces a fine violet colour which gradually passes into blue. Mercuric chloride produces the same effect. A solution of morintannic acid gives a yellow precipitate with *gelatin*, a greenish precipitate with *ferroso-ferric sulphate*, a yellow with *acetate of lead*, and yellowish-red with *stannous chloride*.

Moric acid or *morin*, as already stated, is nearly insoluble in cold water, and is only slightly dissolved by boiling water. It requires 4,000 parts of water at 20° C., and 1,060 parts at 100° C. to dissolve it. It dissolves readily in strong alcohol, from which solution it is reprecipitated on the addition of water. It is insoluble in carbon bisulphide, and only slightly soluble in ether. It combines with, and is dissolved by, alkalis, forming a yellow solution, from which it is precipitated by acids. Ferric chloride added to an alcoholic solution of moric acid produces an olive-green colouration.

According to Goppelsroeder, a solution of moric acid may readily be distinguished from morintannic acid by the addition of a minute quantity of aluminium sulphate, which causes the former to become highly fluorescent, whilst morintannic acid is not affected. A solution of an alkaline morate, treated with sodium amalgam, at first becomes blue, then green, and finally yellowish-brown. At this stage it no longer gives a precipitate on the addition of an acid, since the moric acid has been converted into phloroglucin. The change may be represented by the following equation:—



(Moric acid)

(Phloroglucin).

A solution of moric acid or alkaline morate is not precipitated by gelatin although it stains animal matter yellow. Ferric chloride, according to Wagner, colours the solution garnet-red; but Hlasiwetz and Pfaundler found it to give an olive green colouration.

According to Löwe, fustic contains three colouring matters, viz., morin, maclurin, and morintannic acid. He found morintannic acid to contain an atom less of oxygen than maclurin.

W. M. Gardner* has recently compared the dyeing properties of morin and maclurin. He finds morin to give considerably deeper shades with chromium and aluminium mordants, but lighter shades with iron mordants than maclurin.

* *The Dyer*, 1892, p. 46.

A decoction of fustic gives the following reactions :—

Alkalies,	Orange-yellow to yellow-brown colour.
Weak acids,	Slight pale yellow precipitates.
Alum,	Bright yellow precipitate.
Acetate of lead,	Yellow-orange precipitate.
Acetate of copper,	Brownish-yellow precipitate.
Ferrous sulphate,	} At first, olive colouration ; on standing, a dark brownish-olive precipitate.
Ferric sulphate,	
Stannous chloride,	Rich brown-yellow precipitate.
Copper sulphate,	Dark green precipitate.
Gelatin,	Yellow flocculent precipitate.

Fustic is used in the dye-house in various forms ; as chipped and rasped wood ; as an aqueous extract ; as a paste ; and to a certain extent, as a dry or solid extract.

Fustic is one of the most important of all yellow colouring matters, especially for wool and worsted. It is very extensively used in conjunction with logwood for dyeing black, and together with logwood, alizarin, and other colouring matters, for numerous compound shades, *e.g.*, browns, olives, drabs, &c. In all such cases the general mordant is bichromate of potash or soda. For the production of bright yellow shades *tin* or *aluminium* mordants are used. These bright yellows, however, although fairly fast to milling, are soon changed on exposure to light. They become much browner. Fustic gives the following series of shades with the various mordants :—

Chromium mordants,	Olive-yellow to brownish-yellow.
Aluminium,	Yellow.
Iron,	Dark-olive.
Copper,	Olive.
Tin,	Bright yellow to orange-yellow.

Dyeing of Cotton.—Fustic is applied to cotton much in the same manner as logwood. It is used principally for compound shades. Fustic as a yellow is not much employed for cotton, and where formerly used has been superseded by chrysamin and similar dyes. Fustic is of considerable use in the dyeing of catechu shades.

Dyeing of Wool.—In the heavy woollen district fustic is used in very large quantities in conjunction with logwood, indigo, and alizarin colours. In such cases the mordant is invariably bichromate of potash, although ferrous sulphate is often used as a saddening agent. The bichromate of potash is applied to the extent of from 2 to 4 per cent. previous to dyeing, as already described under logwood. When the red woods are used for fast browns, which, however, is now not often the case, the bichrome is applied after dyeing. In such cases considerably more fustic is required to produce a given shade than where the wool is mordanted before dyeing. In the dyeing of drabs and browns with fustic, logwood, madder, &c., it is customary to use a little sumach. The principal object appears to be that in conjunction with copperas it helps to sadden the shade, but its utility is questionable. The tannin which it contains imparts a harsh

feel to the wool, and, furthermore, interferes with the dyeing properties of logwood. Taking all things into consideration, fustic dyed upon a chromium mordant is still the best yellow colouring matter which the dyer possesses. It is fast to milling and soaping, and stands light well. On exposure to light the shade becomes browner, but in many compound shades the change is not readily noticeable. The so-called alizarin-yellows, galloflavin, &c., are certainly not superior in this respect. Fustic yields the brightest shade with stannous chloride as the mordant. Either separate baths or one bath may be used, as in the case of cochineal. The single bath method gives the best results. A good yellow is obtained with 4 per cent. of stannous chloride, 4 per cent. of oxalic acid, and 50 per cent. of fustic. The addition of a little gelatin is beneficial, since it precipitates the tannin of fustic, and thereby yields brighter shades. A larger quantity of tin salts gives still brighter yellows, but it is objectionable on account of the harsh "handle" which the wool acquires. In practice these bright yellow shades are now seldom dyed with fustic. Fustic and the other natural yellow colouring matters have been to a great extent replaced by the artificial dyestuff, tartrazin—a colour which stands the action of light remarkably well. As mentioned under cochineal, fustic is used in conjunction with that colouring matter for dyeing scarlets and oranges.

Dyeing of Silk.—Fustic is not used in silk dyeing for the production of yellow shades, but it finds application for shading certain blacks (see p. 357), as well as for olives and browns. It is fixed on silk with iron and copper mordants.

Detection on the Fibre.—In most cases where fustic has been used, the ash will contain chromium. In bright yellows or oranges tin will be found.

The reactions of fustic on the dyed fibre are not very striking, and are very similar to those of quercitron bark and Persian berries.

The table on next page shows the principal reactions of fustic dyed with chromium and tin mordants respectively.

The presence of fustic in many compound shades can only be detected with great difficulty. In many cases its presence may be inferred by negative tests and a knowledge of the other constituents present. In the case of a brown, for example, in which logwood and alizarin-red have been found, if the colour is fast to soap, gives up nothing to alcohol, and shows no characteristic reactions with other re-agents, the yellow part of the shade is most probably fustic. If the material is boiled in acetate of alumina it yields a yellow solution with a green fluorescence. The solution on evaporation with nitric acid becomes red.

Fustin or Wool Yellow is the commercial name of a paste dye obtained by treating the colouring matter of fustic with diazobenzene chloride. It dyes wool either mordanted or unmordanted, and either

in a neutral or an acid bath. The shades are "redder" than those given by fustic and are not so fast to light. (See also *Artificial Mordant Colours*.)

Reagent.	Wool Mordanted with Chromium Salts.	Wool Mordanted with Tin Salts.
Hydrochloric acid, .	<i>Nil.</i>	Yellow solution; colourless on dilution.
Sulphuric acid, .	Little change, solution yellow; on dilution, fibre much lighter, solution colourless.	Solution yellow; which remains yellow on dilution.
Nitric acid, . .	Brown; on addition of soda, red.	Brown; on addition of soda, red.
Stannous chloride, } Hydrochloric acid, } and Water, . . }	Little action.	Little action.
Caustic soda, . .	Fibre brown; solution colourless.	Browner; solution yellow, decolorised on addition of H Cl.
Boiling alcohol, .	<i>Nil.</i>	<i>Nil.</i>
Boiling soap, 1 per cent. solution, .	Solution faintly yellow; fibre redder.	Solution deeper yellow; fibre straw colour.
Boiling sodium carbonate, $\frac{1}{2}$ per cent. solution, . . .	Solution orange - yellow; fibre redder.	As with soap.
Boiling 5 per cent. solution of sulphuric acid, . . .	Solution yellow; fibre much lighter.	Solution yellow; fibre not greatly affected.

QUERCITRON BARK AND FLAVIN.

Quercitron Bark is the inner bark of a species of oak, the *Quercus nigra* or *Quercus tinctoria*, a native of America. It grows abundantly in Pennsylvania, Georgia, and the Carolinas. The best qualities are imported from Philadelphia, New York, and Baltimore. Bancroft, in 1775, first made known the dyeing properties of quercitron bark, and by an Act of Parliament obtained exclusive right of importing it for a period of six years.

The bark is removed from the tree, dried, ground between mill-stones, and comes into the market as a mixture of woody fibre and fine powder, of a yellow or buff colour. As a rule, the more of the fine powder present, the greater the value of the sample, since the woody portion, which is not easily reduced to powder, contains only a small quantity of colouring matter.

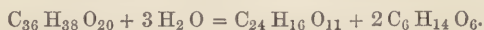
The colouring principles of quercitron bark are known as *quercitrin*

and *quercetin*, and were first investigated by Chevreul. He also found it to contain a peculiar tannin, which has since been named quercitannic acid.

Quercitrin, $C_{36}H_{38}O_{20}$, may be obtained in the pure state by boiling quercitron bark with alcohol and precipitating the tannin by means of gelatin. The solution is then concentrated by evaporation, and the crystals which separate recrystallised from boiling alcohol. It may also be easily prepared from some varieties of flavin which consists of nearly pure quercitrin. On boiling with water and filtering, the solution on cooling deposits quercitrin in the crystalline form.

Quercitrin forms pale yellow crystalline needles possessing a feeble acid reaction. It is but slightly soluble in cold water, but dissolves more freely in boiling water. It is nearly insoluble in ether, but readily soluble in alcohol. Alkaline solutions dissolve quercitrin readily with a greenish-yellow colour, which becomes brown on exposure to the air. An aqueous solution gives bright yellow precipitates with acetate of copper and lead and with stannous chloride.

Quercitrin is a glucoside, and when boiled with dilute sulphuric acid splits up into quercetin, and a species of sugar, isodulcite. The reaction may be represented by the following equation :—



Quercetin, $C_{24}H_{16}O_{11}$, crystallises in needles of a bright yellow colour. It is insoluble in cold, and only sparingly soluble in hot water, but readily dissolves in alcohol and in acetic acid. It is very sparingly soluble in ether. It dissolves in alkalies with a deep orange-yellow colour, which becomes dark brown on being treated with sodium-amalgam. An alcoholic solution of quercetin gives orange precipitates with salts of calcium, barium, and lead. When dry quercetin is treated with concentrated sulphuric acid it forms a sulphonic acid, and the solution on dilution dyes wool a yellow without a mordant.

A freshly-made decoction of quercitron bark is transparent and of a dull orange-red colour, but in a short time it becomes turbid and deposits a yellow crystalline mass. The supernatant liquid acquires at the same time a redder colour, and the colouring matter is gradually destroyed. This decomposition is probably brought about by a ferment which splits up the glucoside. A decoction of quercitron bark, consequently, should only be prepared as required for immediate use. The decoction gives the following reaction :—

Alkalies,	Deepen the colour.
Acids,	Brighten the liquid and form a brown flocculent precipitate.
Alum,	Brightens the solution and forms a slight yellow precipitate.
Stannous chloride,	Brown precipitate.
Stannic chloride,	Yellow precipitate.
Acetate of lead,	Brownish-yellow flocculent precipitate.

Acetate of copper,	. . .	Olive-green precipitate.
Iron salts,	. . .	Olive-brown precipitate, forming slowly.
Gelatin,	. . .	Reddish flocculent precipitate.

Flavin is the name given to a preparation of quercitron bark. It is very much stronger, and yields brighter shades than the original bark. It comes into the market in the form of a very fine powder of a buff or brown colour. Flavin varies considerably in composition, according to the mode of preparation. It consists, as a rule, of a mixture of quercitrin and quercetin, with more or less woody fibre; but some specimens consist of nearly pure quercitrin, while others contain quercetin only. The best qualities of flavin are imported from America, where it is probably prepared from the fresh bark; but the details of the manufacture are kept secret. One method of preparation consists in boiling 100 parts of ground quercitron bark with 300 parts of water and 15 parts of sulphuric acid for some hours. After cooling, the mixture is run on to woollen filters, and the paste washed until free from acid. It is then dried and ground. The tinctorial power of good flavin is 12 to 20 times as great as that of quercitron bark. Practically an ounce of flavin is equal to about a pound of quercitron bark.

In addition to the preparation flavin, quercitron bark is also used by the dyer in the form of extracts, known commercially as *bark-liquor* or *bark-extract*.

Dyeing.—Quercitron bark gives on mordanted cloth very similar shades to fustic, and the methods of application are essentially the same. Speaking generally, chromium mordants give rather redder shades with quercitron bark; aluminium mordants, paler yellows; and tin mordants brighter and redder yellows. The extracts and flavin are much more extensively used in dyeing than the bark itself. Bark-extracts are used to a considerable extent in cotton dyeing, and comparatively large quantities are used in woollen printing. Flavin is used principally in wool dyeing either alone or in conjunction with cochineal for scarlets and oranges by the single bath process. Silk is dyed principally with flavin on aluminium mordants with the addition of some tin salt in order to make the shade more brilliant. The bright yellows produced by flavin and quercitron bark are acted upon by light in a similar manner to those dyed with fustic—*i.e.*, they become reddish-brown.

As mentioned under fustic, tartrazin is far superior as regards fastness to light, although the natural colouring matters are much faster to milling and scouring.

Detection on the fibre.—The colouring matter of quercitron bark on the fibre gives similar reactions to fustic. The following are the principal reactions:—

Reagent.	Chromium Mordant.	Tin Mordant.
Hydrochloric acid, .	Solution <i>nil</i> ; fibre slightly browner.	Yellow solution; colourless on dilution.
Sulphuric acid, .	Fibre little changed; solution yellow; on dilution solution colourless; fibre much lighter.	Yellow solution; remains yellow on dilution.
Nitric acid, . .	Brownish-yellow; red with caustic soda.	Orange yellow; red with caustic soda.
Stannous chloride and Hydrochloric acid, .	Little action.	Little action.
Caustic soda, . .	Fibre browner; solution colourless.	Fibre browner; solution yellow.
Boiling alcohol, .	<i>Nil</i> .	<i>Nil</i> .
Boiling soap, $\frac{1}{2}$ per cent. solution, .	Little affected.	Solution faintly yellow; fibre browner, but not much lighter.
Boiling sodium carbonate, $\frac{1}{2}$ per cent. solution, . .	Little affected.	Yellow solution; fibre brown-yellow.
Boiling sulphuric acid, 5 per cent. solution, . . .	Solution slightly coloured yellow; fibre much lighter.	Solution yellow; fibre not much affected.

WELD.

Weld is botanically known as *Reseda luteola*, which is a variety of mignonette. It was formerly cultivated in England, and is still grown in France and other parts of the Continent. It is an herbaceous plant and grows to a height of about 3 feet. The upper part of the plant, especially the leaves and the seeds, contain the most colouring matter, but the stem is also used in dyeing. Weld comes into the market in the form of sheaves or bundles. It was formerly used to a much greater extent than at present. It has been largely superseded by quercitron bark and flavin. Of late years the greatest amount of weld has been used in dyeing cloth for Government contracts, but tartrazin and similar yellows are taking its place. The colouring principle of weld is *luteolin*, which was first investigated by Chevreul. *Luteolin* forms pale yellow needles. It is very soluble in alcohol, by which solvent it may be readily extracted from the plant. It is only slightly soluble in water, either hot or cold, but dissolves readily in alkalies with a deep yellow colour. It dissolves in concentrated sulphuric acid, and is reprecipitated unchanged on the addition of water. On fusion with caustic potash, luteolin forms protocathechuic acid and phloroglucol.

A fresh decoction of weld has a pale yellow colour, but soon becomes turbid and forms a greenish-brown deposit. The solution is slightly acid and gives the following reactions :—

Alkalies,	Colour of solution becomes golden-yellow.
Barium hydrate,	Beautiful yellow flocculent precipitate.
Alum,	Slight yellow precipitate.
Stannous chloride,	Yellow precipitate.
Acetate of lead,	" "
Ferric sulphate,	Olive-brown colouration ; on standing a brown precipitate forms.
Copper acetate,	Yellow-brown precipitate.
Acids,	Give a turbidity.
Potassium bichromate,	Golden-yellow colouration, on standing yellow precipitate.

Dyeing.—Weld gives with chromium mordants olive-yellow shades ; with alumina greenish-yellow ; with tin bright yellow ; with iron olive, and with copper mordants yellow-olive shades. The properties of weld appear to have been overlooked by dyers. It may be considered superior to all natural yellow colouring matters in regard to fastness to light, and is certainly inferior to none as regards fastness to milling. Weld is not much used in cotton dyeing, although, with chromium mordants, it yields a yellowish-olive shade which is very fast to soap and light. For silk it is certainly the best natural yellow, but has been practically superseded by the coal-tar yellows.

The methods of application for weld are practically the same as those for fustic and quercitron bark. Since its colouring power is small, larger quantities of weld are required. It is principally dyed on aluminium mordants, which should be free from iron, since even traces of this metal dull the colour. The dye-bath is prepared by introducing the requisite amount of weld chopped into small fragments, and enclosed in canvas bags and boiling for about half an hour. The bath should only be prepared as required.

Detection on the Fibre.—The reactions given by weld on the fibre are very similar to those of quercitron bark and fustic. Dyed upon a tin mordant, the fibre is little affected by either dilute acids or alkalis. With stannous chloride and hydrochloric acid the fibre becomes rather redder, whereas fustic and quercitron bark are not appreciably affected. With strong sulphuric acid, the fibre is turned yellowish-olive, and, on addition of water, is almost decolorised.

PERSIAN BERRIES.

Persian berries are the fruit of the buckthorn and of several species of *Rhamnus*, shrubs growing wild and also cultivated in Southern Europe and the East. The product of the *Rhamnus amygdalinus* yields the best quality. The berries are usually gathered before they are

quite ripe, which causes them to have a yellowish-green shrivelled appearance. On being kept for a few years, they become browner and deteriorate in value, especially if allowed to remain in a damp place. Persian berries possess a disagreeable bitter taste. The colouring principle of Persian berries exists in the form of a glucoside. This glucoside, known as *xanthorhamnin*, also as *chrysorhamnin*, may be extracted from the berries by means of alcohol and purified by recrystallisation. It forms golden-yellow needles soluble in water and alcohol, but insoluble in ether. It is decomposed on boiling with dilute sulphuric acid into *rhamnetin* and a species of sugar. The same effect is produced by heating the compound to about 150° C.

Rhamnetin crystallises in microscopic yellow needles. It is only sparingly soluble in water. *Xanthorhamnin* and *rhamnetin* bear a close resemblance to quercitrin and quercetin, and according to Hlasiwetz and Bolley, they are identical.

A freshly-prepared decoction of Persian berries gives the following reactions :—

Alkalies,	Change the colour to orange.
Acids,	Solution rendered turbid.
Acetate of lead,	Slowly produces a yellow precipitate.
Sulphate of copper,	Greenish-yellow solution.
Ferric sulphate,	" " "

Persian berries, like quercitron bark, are used principally in the form of extracts. They are used to a considerable extent in calico-printing for yellow, orange, and green shades. In wool dyeing they have a limited use in conjunction with tin mordants for producing bright yellows and oranges, but, like the other natural yellow colouring matters, the shades turn brown on exposure to light. They are of more use for producing oranges and scarlets with cochineal than for pure yellows; but are more expensive than fustic or quercitron bark, and possess no advantage. Persian berries are also used in woollen printing. Copper mordants give with Persian berries a yellowish-olive shade, which is very fast to light. On exposure the shade becomes greener and actually increases in intensity. Hummel has found that after exposure for twelve months such an olive does not fade.

Persian berries dye redder and deeper shades than either fustic or quercitron bark.

Chromium mordants give brown.

Aluminium	"	"	bright yellow.
Tin	"	"	orange.
Iron	"	"	dark olive.
Copper	"	"	yellowish-olive.

Detection on the Fibre.—The reactions of this colouring matter on the fibre are not sufficiently characteristic to distinguish it readily from quercitron bark. With stannous chloride and hydrochloric acid

the fibre becomes yellower, whereas quercitron is not much affected and weld becomes redder.

YOUNG FUSTIC OR FUSTET.

This dyestuff is the wood of *Rhus cotinus*, a small tree growing in the West Indies and also in the southern parts of Europe. It belongs to the same genus as the sumach tree and is quite distinct from *old fustic*. The colouring principles of young fustic have recently been investigated by J. Schmidt.* He finds young fustic to contain a substance which is easily broken up by dilute acids or alkalies into a tannin and a glucoside. The glucoside named *fustin* is readily soluble in boiling water, alcohol, and alkalies; but only sparingly soluble in ether. When warmed with dilute sulphuric acid fustin is decomposed into a sugar and fisetin.

Fisetin crystallises in small lemon-yellow prisms having a composition very similar to quercitrin and closely resembling that compound in its reactions.

A decoction of young fustic oxidises on exposure to air, becoming of an orange-brown colour. A fresh solution of the colouring matter gives the following reactions:—

Alkalies,	Solution becomes orange.
Acids,	„ „ greenish.
Lime water,	Orange precipitate.
Stannous chloride,	„
Lead acetate,	„
Copper acetate,	Dark red precipitate.
Ferric sulphate,	Olive-green „

Young fustic has a limited use in wool dyeing, principally for oranges and scarlets with cochineal; but it is not so good as either fustic or quercitron bark. The shades yielded by young fustic and the various mordants are very similar to those of quercitron bark. With bichromate of potash the shade is much redder, resembling that given by Persian berries. Young fustic is neither so fast to milling nor light as any of the other natural yellow colouring matters described, and at the present day it has practically fallen into disuse.

Detection on the Fibre.—Young fustic on wool gives the following reactions:—

Sulphuric acid,	Fibre orange, solution yellow; colourless on dilution.
Hydrochloric acid,	Fibre unchanged, solution yellow.
Nitric acid,	Fibre dark brown.
Stannous chloride and Hydrochloric acid,	Solution faintly yellow.
Caustic soda,	„ yellow.

* *Journ. Soc. Dyers and Col.*, 1886, p. 148.

TURMERIC.

Turmeric, also known as Indian saffron, is the underground stem of *Curcuma tinctoria*, a plant growing abundantly in the East Indies and China. The tubers or roots are externally of a greenish-yellow colour, but internally the colour is deep yellow or orange. They possess a strong odour and an aromatic, bitter taste. The roots are ground, yielding a bright orange powder, which should be kept dry; otherwise, if exposed to a damp atmosphere, the colour is deteriorated. Turmeric only yields a small amount of its colouring matter to cold water; hot water extracts a larger quantity, whilst alcohol dissolves it freely.

The colouring principle was first isolated by Vogel and Pelletier, who named it *curcumin*. It may be prepared by first extracting the ground root with carbon bisulphide in order to remove the volatile oils and resinous matters. The residue is then treated with dilute caustic soda and the solution acidulated with hydrochloric acid, when the colouring matter is precipitated in yellow flakes. After drying, it may be dissolved in ether and recrystallised. After treating with carbon bisulphide the colouring matter may also be obtained by extracting the residue with dry ether. Pure curcumin forms light yellow prismatic crystals which melt at 178°C . It is only slightly soluble in water, but readily soluble in alcohol and ether. It dissolves in alkalies with a deep reddish-brown colour. In this respect turmeric is very sensitive, and paper saturated with a solution of turmeric is frequently used as a test for alkalies. The most characteristic reaction of curcumin and turmeric is with boric acid. If a piece of filter paper stained with a solution of turmeric be moistened with boric acid and dried, it becomes brownish-red; and on now adding a drop of caustic soda it is turned blue or green.

Turmeric is a substantive dye for cotton, wool, and silk and is used almost entirely in dyeing compound shades. The colour is fugitive to light and is easily affected by soap and weak alkalies. Notwithstanding, large quantities are still used in dyeing cotton, wool, and silk. Although mordants are unnecessary, yet they modify the shade. Bichromate of potash gives a browner shade; alum a brighter; stannous chloride, bright orange, and ferrous sulphate, olive.

Cotton, wool, and silk are usually dyed with turmeric, without any further addition, or with a little alum, acid, or acid salt. If the bath is in the least degree alkaline, the fibre is not dyed. It is important that the temperature does not rise much above 60°C ., otherwise, the shade is both duller and lighter. This is especially the case when no acid is used in the dye-bath.

Detection on the Fibre.—Turmeric gives the following characteristic reactions on the fibre :—

Sulphuric acid, . . .	Fibre and solution reddish-brown; on dilution, fibre pale straw; solution colourless.
Hydrochloric acid, . . .	Fibre reddish-brown; solution, pale pink; on dilution, fibre bright yellow.
Nitric acid,	At first deep red, then yellow.
Caustic soda,	Bright reddish-orange fibre and solution.
Boiling 5 per cent. solution of sulphuric acid,	Pale yellow solution; fibre paler; red-orange on addition of caustic soda.
Boiling $\frac{1}{2}$ per cent. solution of sodium carbonate,	Orange solution; fibre light brown.
Boiling alcohol,	Yellow solution, green fluorescence.

In a compound shade turmeric may be detected by boiling with alcohol, adding water and evaporating nearly to dryness with a little wool; and testing the dyed wool as above. Or the alcoholic solution may be concentrated and poured on to a filter paper, and the boric acid test applied as described above.

THE RED WOODS.

These dyewoods may be divided into two classes, viz., the soft woods and the hard woods, also known as the open and close woods respectively. The colouring matter of the *former* class is easily and freely soluble in water; hence extracts of the woods may be readily prepared. The hard woods, on the contrary, being of a more resinous nature, yield their colouring matter but slowly and imperfectly to water. Extracts of these woods cannot be economically prepared on account of the sparing solubility of the colouring matter.

BRAZIL, PEACH, LIMA WOOD, &c.

Soft or Soluble Class of Red Woods.

The soft or soluble class are all obtained from various species of the genus *Cæsalpinia*, belonging to the natural order *Leguminosæ*. The principal varieties are Brazil wood, Peach wood, Sapan wood, Lima wood, and Pernambuco wood. They are imported into this country in the form of crooked and knotty logs, of a dark red colour externally, but nearly colourless in the interior. They possess a slightly aromatic odour and a bitter sweet taste.

Brazil wood is the product of a tree botanically known as *Cæsalpinia brasiliensis*, which grows in the forests of Brazil. It is one of the best of the class, but is now somewhat scarce.

Peach wood, also known as Santa Martha wood, is the product of *Cæsalpinia echinata*, a native of Mexico. The best quality comes from Nicaragua, and an inferior wood is imported from Sierra Nevada.

Sapan wood, the product of *Cæsalpinia Sappan*, is imported from Siam, Japan, and East Indies.

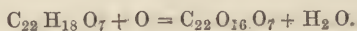
Lima wood, a variety of sapan or peach wood, is imported from Peru.

In addition to these woods there are various other species sold in the market, but they are not of great importance, and closely resemble one another. All these woods dye very similar shades with the various mordants, and it would appear that they contain one and the same colouring principle. This colouring principle, which is named *brazilin*, does not exist as such in the fresh wood; but is present in the form of a glucoside, a body which, in itself, possesses no dyeing properties. By the action of a peculiar ferment, assisted by a moist atmosphere, the glucoside splits up into *brazilein* and glucose or sugar. This may be proved as follows:—If a decoction of fresh Brazil wood is boiled with a solution of the double tartrate of potash and copper no precipitation takes place, but if the liquid be first boiled with dilute hydrochloric acid or sulphuric acid and then boiled with the copper solution, an abundant red precipitate of cuprous oxide is thrown down, showing the presence of glucose. The boiling with weak acid has the same effect as the ferment, but it acts much more quickly. The fresh decoction gives no precipitate with acetate of lead, but after it has been boiled with acid, a precipitate of a brilliant red colour is obtained by this reagent. If the solution which has been boiled with an acid is neutralised and treated with an alkaline salt, beautiful reddish crystals are deposited on cooling.

The decoctions of the fresh woods can be exposed to the air for a considerable length of time without undergoing any change. The colour of the liquid remains a bright yellow, but if the rasped wood is exposed to the air, especially when moist, it soon changes its original colour and becomes red. The change is one of oxidation, and up to a certain point the wood gains in tinctorial value; but the operation requires attention, otherwise the colouring matter is liable to be destroyed. It is not so readily damaged as the colouring matter of logwood. The changes which take place are quite analogous to those which occur during the fermentation of logwood. The glucoside, in the first place, splits up into *brazilin* and glucose, and the *brazilin* is then converted by oxidation into *brazilein*, which is the real colouring matter required. Dinger's process consists in adding 4 lbs. of gelatin, dissolved in water, to every cubic yard of ground wood, and allowing the whole to ferment for several days. Wood so treated is said to yield a stronger extract than that obtained in the ordinary way. No doubt the ammonia evolved during the decomposition of the gelatin facilitates the oxidation of the *brazilin*. It has been proposed to add a little chlorate of potash to the hot extract with the object of increasing its brilliancy. The glucoside of Brazil wood is but imperfectly known; it has been obtained with difficulty by Schutzenberger as a non-crystallisable substance readily soluble in water and alcohol.

Brazilin was first isolated and studied by Chevreul. It may be obtained from Brazil wood by the method employed for the preparation

of hæmatoxylin from logwood. According to Kopp, the formula for brazilin in the anhydrous state is $C_{22}H_{18}O_7$. The crystals when pure are nearly colourless, and are freely soluble in water, alcohol, and ether. On exposure to air brazilin quickly absorbs oxygen, becoming thereby converted into brazilein. The change takes place more rapidly in the presence of a trace of ammonia. It may be expressed by the following equation :—



This reaction is analogous to the formation of hæmatein by the oxidation of hæmatoxylin. Brazilin, by the action of nitric acid, is partially converted into picric acid.

Brazilein, $C_{22}O_{16}O_7$, is produced by the oxidation of brazilin. According to Hummel and Perkin, it may be obtained in a pure state in the following manner :—A concentrated decoction of Brazil wood is made slightly alkaline by ammonia, and exposed to the air for two or three days with occasional stirring. A dark purple precipitate of the ammonia compound of brazilein is formed, which is collected on a filter and well pressed. The precipitate is dissolved in hot water and treated with an excess of acetic acid. After heating the mixture for some time, it is cooled and filtered. The filtrate on evaporation deposits minute crystals of brazilein, which are collected on a filter and washed, first with acetic acid, then with pure water. Brazilein thus obtained has the form of very minute dark crystals which have a grey metallic lustre ; when crushed they give rise to a brown-red powder. It is but slightly soluble in cold, but freely in hot, water ; the solution having a pale yellowish-pink colour with a greenish fluorescence. Pure brazilein dyes wool much brighter shades than the wood extracts. Brazilein slowly dissolves in concentrated sulphuric acid, forming brazilein-sulphonic acid. By the action of concentrated hydrochloric and hydrobromic acids it forms crystallisable compounds which have greater tinctorial power than the brazilein itself. It is reduced to colourless brazilin by treatment with bisulphite of soda or with zinc dust.

The following are the most characteristic reactions of decoctions of Brazil wood, peach wood, &c. :—

Weak acids—solution yellow or orange.

Strong hydrochloric acid turns the solution bright pink, which, however, disappears on addition of water.

Alkalies give a crimson-red tint.

Potassium bichromate gives a dark red liquor, which on standing deposits a deep red precipitate.

Neutral acetate of lead gives only a slight reddish precipitate.

The filtered liquor dyes a deeper and brighter shade than the original solution. It appears, therefore, that this reagent removes only those substances which injure the beauty of the colour.

Basic acetate of lead gives an abundant bluish precipitate.

Alum gives a red colouration.

Basic alum gives a beautiful pink-red precipitate.

The lakes produced by decoctions of Brazil wood, &c., and basic alum are used by decorators and paper-stainers under such names as Venetian, Florence, or Berlin lakes.

Application.—Brazil wood and allied woods are used by the dyer both in the form of chips or raspings and extracts of various degrees of strength. At the present day, however, on account of their fugitive character, they are not used to any great extent. They serve chiefly to modify the shades produced mainly by other colouring matters. The woods were formerly used to a considerable extent in calico-printing for producing pinks and purples; but the same shades can be obtained far faster by means of the alizarin dyes. Crimson shades may be obtained by these woods similar in shade to those produced by cochineal; but they are not nearly so fast.

The colouring matter of the red woods, like that of logwood, cannot be fixed upon the fibres without the aid of a mordant, which develops and determines the shade.

With the more important mordants the shades produced are :—

Chromium salts,	Violet to claret.
Aluminium „	Rose-reds.
Iron „	Greyish-violet to purple.
Copper „	Drab to brown.
Tin „	Crimson-red.

All these shades are fugitive to light, and are more or less easily removed by soaping. They are faster on wool than on cotton.

Dyeing of Cotton.—The cotton is prepared by steeping some hours in a decoction of sumach, or other tannin matter, and is then worked in a cold solution of basic alum, prepared by adding sodium carbonate to a solution of ordinary alum. The material is then washed and dyed in a fresh bath with a decoction of the wood. The shade obtained is a dull bluish-red. The alumina may also be fixed on the fibre by padding the cotton with aluminium acetate. If the cotton, after being prepared with tannin, is worked in a solution of stannic chloride instead of alum, a brighter and yellower shade, approaching scarlet, is obtained. Peach wood is used to a considerable extent in Lancashire, in piece-dyeing for browns, olives, &c., in conjunction with cutch, logwood, and fustic.

Dyeing of Wool.—In most cases it is preferable to mordant first and dye in a separate bath. According to the depth of shade required, from 1 to 3 per cent. of bichromate of potash may be used. With a small quantity of the woods a dull violet shade is obtained, but larger amounts give a good claret. If sulphuric acid be added to the mordanting bath the shade subsequently obtained is redder. A bluish-red shade, inclined to crimson, is obtained by mordanting the wool with 8 per cent. of alum and 8 per cent. of tartar, and dyeing in a separate bath with about 50 per cent. of Brazil wood, or other similar wood. (Good results may also be obtained by the single bath

method). An addition of calcium acetate to the dye-bath is beneficial. Brighter shades are obtained by adding a little stannous chloride to the mordanting, as well as gelatin to the dye-bath. The effect of the gelatin is to precipitate tannin matters derived from the wood.

By mordanting with 2 per cent. of stannous chloride and 10 per cent. of tartar, and dyeing with 40 to 50 per cent. of wood, a bright red shade is produced. In order to obtain the maximum effect, however, it is necessary to use a very large amount of tartar.

Dyeing of Silk.—These dyewoods are almost entirely replaced by the artificial colours in silk dyeing. The general method of application was mordanting with alum or tin salt, and dyeing in a fresh bath. With tin salts, the single bath method is also applicable.

Detection of the Red Woods on the Fibre.—The mordant is detected by burning the fibre, and testing the ash in the way described under logwood. Boiled with a 1 per cent. solution of soap, most of the colour is removed from cotton, which distinguishes these reds from alizarin. Immersed in a cold solution of *caustic soda*, the colour is removed and turned violet. Concentrated *sulphuric acid* turns the fibre brown, and the solution yellow to brown. The colour of the fibre is turned yellow by immersion in a mixture of *stannous chloride* and *hydrochloric acid*, which distinguishes this class of woods, from barwood, &c. Boiling *alcohol* is coloured yellow, whereas archil imparts a bluish-red colour to alcohol.

SAUNDERS-WOOD, BARWOOD, AND CAMWOOD.

Close or Insoluble Class of Red Woods.

The principal woods of this class are saunders-wood, camwood, and barwood. They yield much faster colours than the "open" or soluble class, but the colouring matter is very sparingly soluble in water. On this account extracts are not prepared; the wood itself in a rasped state being used in all cases of dyeing. Although the shades which these woods yield vary somewhat in tone, their properties are so similar, that it is highly probable all contain one and the same colouring principle.

Saunders-wood (known also as *sandal wood*, *santal wood*, and *red sanders*) is the product of *Pterocarpus santalinus*, a tree growing in India, Ceylon, and other tropical parts of Asia and also in Madagascar. It is imported in logs which are very hard, compact, and of high density. The exterior is of a dark brown colour, whereas the interior is red. It yields to alcohol about 16 per cent. of an extract which is insoluble in cold, and only very slightly soluble in hot water.

Barwood is the product of *Baphia nitida*, a large tree which grows extensively in Sierra Leone. It yields about 23 per cent. of extract to alcohol. Boiling water extracts about 7 per cent. of colouring matter, but it is almost entirely precipitated on cooling.

Camwood, or kambe wood, is also imported from the west coast of

Africa. It yields its colouring matter somewhat more freely than the other two woods. Its price is considerably higher than barwood and saunders-wood, but it is considered superior as regards fastness. It gives also brighter and fuller shades.

The colouring principle of saunders-wood, which, as already stated, appears to be identical with that of barwood, is named *santalin*, and is said to have the formula $C_{15}H_{14}O_5$. It appears to be developed by age, since it is not found in young branches, whilst it exists in large quantities in the trunk. Santalin may be prepared by exhausting saunders-wood with ether. The ether is evaporated and the extract after being boiled with water is dissolved in alcohol, and the solution precipitated by acetate of lead. The precipitate is collected, washed, and decomposed by sulphuric acid in alcohol. The sulphate of lead is removed, when the alcoholic solution deposits santalin in the form of small crystals of a beautiful red colour. Santalin may also be isolated by boiling the rasped wood with water to remove the tannin, and heating the residue with a solution of borax. On the addition of hydrochloric acid a voluminous red precipitate is produced which, after being washed, is dissolved in boiling alcohol; from which solution santalin crystallises out on cooling.

Santalin is practically insoluble in water, but dissolves readily in ether, alcohol, and acetic acid. It dissolves in ammonia, potash, soda, and the alkaline carbonates, phosphates, and borates with a violet-red colour, and is reprecipitated on the addition of an acid. According to Weidel, saunders-wood, in addition to santalin, contains another crystalline body which is colourless. Its solution in alkalies is of a yellow colour, but it rapidly becomes red on exposure to the air. It is probable that this colourless compound, which has been named *santal*, is reduced santalin.

The colouring matter of camwood has not been sufficiently investigated; but although similar in many respects to santalin, it probably is not identical with it. Camwood is ground, treated with water, and "matured" like logwood, but for a shorter period; whereas saunders-wood and barwood are ground and used direct.

The colouring matter of saunders-wood, barwood, and camwood has recently been produced in a soluble form. The principle involved is the same as that which allows indigo to be used in the form of an extract, viz., by conversion into a sulphonc acid. For this purpose A. Zander* treats saunders-wood, or one of the allied woods, with a warm solution of borax or other alkaline salt, and precipitates crude santalin from this solution by means of hydrochloric acid. The dried precipitate powdered is then warmed with concentrated sulphuric acid until a sample ceases to be precipitated on addition of water. The product is then poured into a saturated solution of common salt and the precipitated colouring matter washed with salt solution and dried.

* *Journ. Soc. Dyers and Col.*, 1888, p. 4.

The substance dissolves in either hot or cold water, and dyes wool in an acid bath. The shades produced are said to be as fast as those obtained by the original wood.

An alcoholic solution of saunders-wood or barwood gives the following reactions :—

<i>Excess of water,</i>	. . .	Yellow turbidity.
<i>Potash or soda,</i>	. . .	Dark crimson or purple colouration.
<i>Lime water,</i>	. . .	Brownish-red precipitate.
<i>Dilute acids,</i>	. . .	Deep cherry-red colouration.
<i>Stannous chloride,</i>	. . .	Blood-red precipitate.
<i>Stannic chloride,</i>	. . .	Brick-red precipitate.
<i>Ferrous salts,</i>	. . .	Violet precipitate.
<i>Ferric salts,</i>	. . .	Brownish-red precipitate.
<i>Copper salts,</i>	. . .	" " "
<i>Alum,</i>	. . .	Turbid.
<i>Lead salts,</i>	. . .	Dark violet gelatinous precipitate.
<i>Mercuric chloride,</i>	. . .	Scarlet precipitate.
<i>Tartar emetic,</i>	. . .	Dark cherry-red precipitate.

A solution of camwood differs from saunders-wood and barwood as regards its behaviour with salts of lead and alumina. With *salts of lead* it gives a bright orange-red precipitate, and with *alum* a beautiful red colouration.

Application.—Saunders-wood, barwood, and camwood are used principally in wool dyeing, in conjunction with other dyewoods, for producing various compound shades, especially *browns*. The shades obtained are very fast to soaping and milling, and, on that account, are largely used for dyeing heavy woollen cloths, which have to be severely milled. In many cases of wool dyeing, however, these woods have been superseded by alizarin-red and anthracene-brown, which are much faster to light than the red woods. Camwood, saunders-wood, and barwood, especially the latter, are also largely employed to give a bottom to woollen cloth which is to be afterwards dyed with indigo. Cudbear is often used for this purpose, but barwood or saunders-wood is much to be preferred. Barwood and allied woods are employed in cotton dyeing almost exclusively for producing shades known as "mock" Turkey-reds. They are, however, neither so fast nor so bright as the real Turkey-red obtained by alizarin; and are distinguished from it by yielding part of their colour to soap. The two classes of reds may also be easily distinguished by the action of acids and alkalies.

In silk dyeing the red woods find no application on account of the sparing solubility of the colouring matter.

The shades obtained with these woods vary according to the mordant employed from a dull red to a rich claret-brown. Camwood gives the bluest and brightest shades; saunders-wood the yellowest shades with the same mordants.

The more important mordants produce the following shades with these red woods :—

Mordant.		Camwood.	Saunders-wood.
Chromium salts,	.	Red-violet.	Brown-red.
Aluminium „	.	Red.	Orange-red.
Iron „	.	Violet.	Maroon.
Copper „	.	Brown.	Brown.
Tin „	.	Bluish-red.	Red.

Dyeing of Cotton.—The red woods, as already stated, are used principally in cotton dyeing for producing the so-called “mock” Turkey reds. Barwood is used largely in such cases, but not nearly to such an extent as formerly. There are various methods employed for producing these reds. The cotton may be steeped in a decoction of sumach and then in a solution of barwood spirits (nitro-muriate of tin) at 4° Tw. It is then well washed and dyed in a boiling bath containing 100 to 200 per cent. of ground barwood. The cotton is entered into the dye-bath at a low temperature, and the liquor gradually raised to the boiling point. Another method is to work the cotton in a cold solution of stannate of soda at about 5° Tw., wring, and work for a few minutes in a solution of alum or of sulphuric acid at $\frac{1}{2}$ ° Tw. The cotton is then well washed and dyed as before. The cotton may also be prepared by working it in a solution of nitro-muriate of tin (6° Tw.), and fixing the mordant in a fresh bath containing sodium carbonate. The nitro-muriate of tin or barwood spirits is prepared by dissolving 4 lbs. of granulated tin in a mixture of 5 gallons hydrochloric acid at 32° Tw., and 1 gallon of nitric acid at 64° Tw. (See also p. 286.)

A fairly good red is obtained on cotton by working it in a cold solution of basic alum at 6° Tw., and fixing the mordant by means of phosphate of soda.

Dyeing of Wool.—The red woods may be applied to wool in the same manner as logwood, viz., by mordanting first and dyeing afterwards; but the best results are undoubtedly obtained by the so-called “stuffing and saddening” process. In practice this method is usually adopted. The wool is boiled for 1 to 2 hours with 20 to 60 per cent. of barwood or camwood; and afterwards boiled without washing in a fresh bath, with 2 per cent. of potassium bichromate, for half an hour. The potassium bichromate may also be added to the dye-bath, but it is preferable to use a fresh bath. In the dyeing of camwood-browns or drabs a certain proportion of logwood and fustic, according to the shade required, is added to the dye-bath. Since the colour is developed in the “bichrome” bath, considerable experience is required to adjust the proper proportions and quantities of woods in order to match a given shade. As the dyeing proceeds, the dyer takes out a small sample of

the wool or cloth from time to time and develops it in a small bath of potassium bichromate kept for that purpose. If necessary, a further addition of wood or wood-extract is made to the bath, and the dyeing continued until a small sample develops to the shade required. The bulk is then "saddened" with bichromate of potash, and the goods afterwards washed and dried. In the dyeing of these so-called fast browns experience has shown that bichromate of potash gives better results than bichromate of soda. Instead of bichromate of potash 5 per cent. ferrous sulphate or copper sulphate may be used as the "saddening" agent.

The red woods in conjunction with other dyewoods are sometimes applied to wool in the following manner:—The goods are mordanted with 2 to 3 per cent. of bichromate of potash, and dyed in a fresh bath with the requisite amount of dyewoods, and then "saddened" with 3 to 5 per cent. of ferrous sulphate.

These colours are very fast to milling, but are more fugitive to light than the anthracene-dyes. A shade produced by camwood or saunders-wood, logwood and fustic, appears to be considerably faster to light than that given by any one of these dyewoods alone.

The brightest shade obtainable by these red woods is given by *stannic chloride* as a mordant, but such a very large amount of tartar is required that it is of little practical interest. By dyeing with 10 to 40 per cent. of red wood, and saddening with 10 per cent. of alum or 1 to 2 per cent. of stannous chloride, fairly good red shades are obtained, but they are not fast to light.

These colouring matters are not suitable for the one-bath system of dyeing.

The close red woods are not used in silk dyeing on account of their sparing solubility, as it is difficult to remove the particles of wood from the silk fibre without deteriorating the material.

Reagent.	Camwood.	Saunders-wood.
Hydrochloric acid, .	Fibre crimson; liquid colourless.	Fibre redder; liquid colourless.
Sulphuric acid (concent.),	Fibre and liquid dark maroon.	Fibre and liquid brown.
Nitric acid,	Brown.	Brown.
Caustic soda (5 per cent.),	Black.	Dark brown.
Stannous chloride, hydrochloric acid, and water, }	Bluish-red.	Redder.
Boiling alcohol, . . .	<i>Nil.</i>	<i>Nil.</i>
Boiling sodium carbonate ($\frac{1}{2}$ per cent.), .	Fibre bluer; solution <i>nil.</i>	Fibre dark grey; solution <i>nil.</i>

Detection on the Fibre.—Dyed on wool the mordant will be usually chromium or iron, or both; on cotton, tin, or, more rarely, aluminium. The foregoing reactions are given by camwood and saunders-wood respectively on the wool fibre.

MADDER.

This well-known dyestuff has been used for dyeing and printing from very early times, but since the introduction of artificial alizarin the amount consumed has decreased greatly. It was formerly considered the most important of all dyestuffs used by calico-printers, but it is now practically entirely displaced by artificial alizarin.

Madder is the root of a plant known as *Rubia tinctorum*, a native of Asia Minor, but it has long been cultivated in Italy, and later in France and Holland. Madder was known as a dyestuff to the ancient Egyptians, and also to the Greeks and Romans, who fixed it upon cotton much in the same manner as is employed at the present day. The *Rubia tinctorum* is a perennial plant which is commercially propagated by shoots. The herbage is cut off and the roots gathered in the third year; in Turkey and the East, however, it is usual to allow the roots to remain in the ground until the fifth or even the seventh year. In this manner the colouring matter is slowly developed by the oxidising influences of the air. In Turkey and Naples the roots are dried in the open air by the sun, but in Holland and France stoves are used for this purpose. Turkey and Naples madders are imported in the root, whilst those from France and Holland are ground.

Fresh roots yield about 25 per cent. of commercial madder. The colouring matter resides almost entirely in the cortical part of the root, little or none being found either in the epidermis or in the central woody part. Dutch and Alsatian madder, after being ground, is usually stored in large casks for two or three years, when the colouring matter is further developed and the tinctorial power increased: but if kept much longer than three years, a further change occurs, resulting in a loss of colouring matter. The best madder is obtained from plants grown on calcareous soils.

On an average 100 parts of dry madder root consist of* :—

Matter soluble in cold water,	55 parts.
„ „ boiling water (alizarin, &c.),	3 „
„ „ alcohol,	1.5 „
„ fibrous,	40.5 „

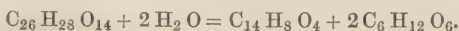
The cold water solution contains from 10 to 15 per cent. of sugar. It also contains two colouring principles—xanthin and chlorogenin—which have the effect of dimming the colour produced by the alizarin.

The principal colouring matters yielded by madder are alizarin, purpurin, and pseudo-purpurin, of which alizarin is by far the most

* Crace Calvert, *Dyeing and Calico Printing*, p. 24.

important. The colouring matter or colouring matters are not contained as such in the fresh madder root, but exist in the form of glucosides, which by the action of a peculiar ferment (also present in the root) split up into colouring matters and sugar. This fact was proved by Schunck in the following manner:—He took some fresh madder roots from the ground, cut them up, and used them for dyeing, when they were found to give the ordinary colours. Another lot of roots, also freshly gathered, were cut up and extracted as quickly as possible with boiling alcohol:—On evaporation, a yellow extract was obtained, which was found incapable of dyeing mordanted cloth any but the very faintest tints, while the parts of the roots which had remained undissolved were equally incapable of dyeing. It is evident, therefore, that the treatment with alcohol had effected a separation of the glucoside and the ferment, which, under ordinary conditions, react to form colouring matter. The alcoholic extract was found to contain the glucoside and the matter insoluble in alcohol to contain the ferment. Schunck named the ferment *erythrozym*. It is insoluble in alcohol, soluble in cold or tepid water, but is coagulated and precipitated on boiling. Schunck found this ferment to be a compound of lime with a nitrogenous substance, and that, if the lime were removed by means of an acid, the erythrozym lost its power of inducing fermentation. This partly explains why it is found advantageous to add a little chalk to the dye-bath when using madder, which contains little or no lime.

Rubian or *Ruberythric acid*, the glucoside existing in the fresh madder root, is sparingly soluble in cold water, more easily in hot water, alcohol, and in ether. It dissolves in alkalies with a blood-red colour. When heated it decomposes at 130° C., giving a sublimate of alizarin. When boiled with dilute acids or by the action of erythrozym (the ferment of madder) it is decomposed into a sugar and alizarin. The change may be represented by the following equation:—



Small quantities of other colouring matters are also formed at the same time.

Alizarin, $\text{C}_{14} \text{H}_8 \text{O}_4$, is the principal and most valuable colouring matter of madder. It was discovered in 1824 by Robiquet and Collin by treating madder with strong sulphuric acid and gently heating the black mass thus formed. It may be more conveniently obtained by extracting madder with alcohol, evaporating the solution to dryness, and treating the residue as follows:—Powder the residue and spread it upon a sheet of filter paper placed on an iron plate. Heat gently, whereupon the extract melts, the paper absorbing the brown resinous bodies; while the alizarin sublimes on the surface of the mass in the form of beautiful orange-red crystals.

Alizarin is now manufactured in enormous quantities from anthracene, a body obtained from coal-tar. (See Part VII.)

Alizarin crystallises in long transparent orange needles. It melts at about 215°C ., and sublimes at a little higher temperature, but partially decomposes, leaving a mass of carbon. It sublimes without decomposition in a current of superheated steam. It dissolves in boiling water to a very slight extent, forming a pale yellow solution. It freely dissolves in alcohol, ether, wood spirit, benzene, turpentine, carbon disulphide, and glycerin. It dissolves in concentrated sulphuric acid, but is reprecipitated unchanged on dilution with water. Alizarin is of a phenolic character and readily dissolves in alkalis with a violet colour. Alum precipitates red or pink lakes; iron salts give purple or black lakes. Barium and calcium chlorides give violet precipitates. Acetate of lead gives a red-violet precipitate. A most interesting reaction of alizarin is that discovered by Græbe and Liebermann, who found that when distilled with zinc it gave anthracene.



It was this reaction which led to the discovery of the process for producing artificial alizarin.

Purpurin, $\text{C}_{14}\text{H}_8\text{O}_5$, another colouring matter of madder, exists, like alizarin, in the fresh root in the form of a glucoside. Purpurin resembles alizarin, but is yellower. It is slightly more soluble in water, communicating to it a pink colour. It dissolves in alkalis with a purple-red colour, which gradually disappears on exposure to the air. The colour of alizarin is permanent in the air. Purpurin is readily detected in minute quantities, and may be distinguished from alizarin by means of the spectroscope.

It may be artificially prepared from alizarin by heating the latter to 160°C . with manganese dioxide and sulphuric acid.

An aqueous decoction of madder has a reddish-brown colour. It gives the following reactions:—

Alkalies,	Bluish-claret solution.
Acids,	Brownish-yellow solution.
Alum,	Brownish-red precipitate.
Stannous chloride,	" "
Iron salts,	Dark brown "
Copper salts,	Red-brown "

Numerous preparations of madder were formerly made; but, since the introduction of artificial alizarin, they have practically fallen into disuse. The preparations are distinguished as *garancin*, *garanceux*, *fleurs de garance*, "*commercial alizarin*," *madder extracts*, &c., but, being at the present day of comparatively little importance, a brief description will suffice.

Garancin is obtained by treating madder with eight or ten times its weight of cold water and allowing the mixture to stand 12 hours. The excess of water is run off, and the pasty mass remaining mixed with sulphuric acid in the proportion of 35 lbs. for every 100 lbs. of

madder originally taken. The mixture is run into a tank, which is then closed, and the whole boiled by means of steam for 4 or 5 hours. A large quantity of cold water is then added, and the mixture run on to woollen filters and the paste washed until free from acid. The paste is collected and submitted to hydraulic pressure, and the cake dried and ground. One hundred parts of madder yield from 30 to 40 parts of garancin possessing a dyeing power four or five times greater than that of the original madder. In this operation two colouring matters, xanthin and chlorogenin, which have the effect of dulling the madder shades, are removed by the maceration in cold water. The treatment with sulphuric acid completes the decomposition of the glucosides, and liberates any colouring matter which may be combined with lime and magnesia. Consequently, there is a considerable gain in colouring power, as well as the production of a purer dyestuff.

Garanceux was obtained from spent madder (*i.e.*, madder which had been used in dyeing) by a similar process to that employed for making garancin. The product was inferior in quality to the garancin obtained direct, and its colouring power about one third.

Fleurs de garance, or flowers of madder, is simply madder which has been treated with dilute sulphuric acid, or even water only, in order to remove the yellow colouring matters, &c. It may be prepared as follows:—100 parts of madder are mixed with 1 part of sulphuric acid and 1,000 parts of water, and allowed to macerate for 10 to 12 hours. The mixture is filtered, and the paste, after washing, submitted in bags to hydraulic pressure, dried and ground. 100 parts of madder yield from 50 to 60 parts of *fleurs de garance*. The aqueous, or acid liquors obtained in this process contain much sugar, and serve for the preparation of an impure spirit. From 100 kilos. of madder about 10 litres of alcohol are obtained.

Dyeing.—With the various mordants madder gives the following series of shades:—

Chromium mordants,	Dull bluish-red to crimson.
Aluminium „	Pink to scarlet.
Iron „	Maroon to reddish-brown.
Copper „	Yellowish-brown.
Tin „	Reddish-orange.

The old method of madder dyeing on *cotton* is practically the same as the application of alizarin (artificial) in Turkey-red dyeing. (See Part VII.)

Madder is used in *wool* dyeing, but not to any great extent, in conjunction with other colouring matters to produce drabs, browns, &c. It is also used by the indigo dyer in the woad vat, but, in this case, madder fulfils the purpose of a ferment rather than a dye. In the dyeing of cotton, madder was formerly a most valuable dyestuff, but, as already stated, it has been practically, entirely, supplanted by artificial alizarin.

In the dyeing of drabs on *wool*, it is usual to dye and mordant in the same bath, using alum and tartar, and modifying the shade with fustic, logwood, &c., as required. In other cases, madder is applied to wool in a single bath, with the mere addition of a little sulphuric acid. Faster and fuller shades are, however, obtained by the two-bath system, mordanting first and dyeing afterwards. The methods of application are similar to those employed for logwood, &c. In mordanting with bichromate of potash deeper shades are subsequently obtained by adding a third of its weight of sulphuric acid to the bath. By using 60 per cent. of madder a rich brownish-red shade is produced. In dyeing with madder upon wool mordanted with alum, it is often necessary to add acetate of lime in order to obtain the best results. A little sumach added to the bath is beneficial, and brighter shades are obtained at 80° C. than at the boiling temperature. At a lower temperature the yellow colouring matters of madder are not so readily fixed. But in any case the red produced by madder and alum mordant is never as bright as that given by alizarin.

In the dyeing of *silk*, madder is scarcely ever used.

Detection on the Fibre.—When dyed upon wool, madder gives the following reactions:—

Reagent.	Chromium Mordant.	Alum Mordant.
Hydrochloric acid, .	Brown.	Little affected.
Sulphuric acid, .	Crimson-yellow on dilution.	Crimson-yellow on dilution.
Nitric acid, . .	Quickly brown, then orange.	Slowly orange.
Stannous chloride and hydrochloric acid, .	Browner.	Brighter.
Caustic soda, . .	Bluer.	Bluer.
Ammonium hydrate,	Bluer.	Slightly bluer.
Boiling alcohol, .	<i>Nil.</i>	<i>Nil.</i>

Boiled with dilute sulphuric or hydrochloric acid, fibre and liquid become orange or orange-yellow, which are turned violet on addition of caustic soda.

In many compound shades it would be practically impossible, or exceedingly difficult, to distinguish between madder and alizarin. This can be readily understood when it is known that the colouring matter of madder is essentially alizarin, and only differs from it in containing small quantities of other colouring principles whose reactions have been little studied.

Cotton dyed Turkey-red with madder behaves in a similar manner with chemical reagents to alizarin. Turkey-red will stand weak

bleaching powder better than many other reds. Stronger solutions decolorise it, but if the cloth is carefully washed and placed in a bath containing madder the original colour will reappear. Turkey-red is not affected, or very slightly, by a boiling soap solution. On treating the cloth with hydrochloric acid it becomes yellow, which turns purple or violet on addition of an alkali. The colour undergoes very little change either by immersion in ammonia or in a mixture of stannous chloride and hydrochloric acid.

ORCHIL AND CUDBEAR.

Orchil and cudbear are manufactured from certain classes of *lichens*, small perennial plants belonging to the class *cryptogamia*. These lichens are found growing in the Canary Isles, Cape de Verde Isles, Sardinia, East Indies, Norway, Madagascar, Zanzibar, and various parts of Central and South America. Formerly the whole of the orchil used in Europe was obtained from Florence. The lichens are commercially known as "weeds," and sold under the names of orchella weed, orchil weed, &c. The two principal species growing on the coasts are the *Roccella tinctoria*, known as "Valparaiso weed"; and the *Roccella fuciformia*, sold as "Lima weed," &c. Of the species growing inland, the *Variolaria orcina* of Auvergne and the *Lecanora tartarea* of Sweden are the most important.

Lichens do not contain any colouring matter already formed, but certain colourless compounds, which, by the action of ammonia and the oxygen of the air, are converted into colouring matters. The principal colour-producing compounds existing in the lichens named are erythrin, lecanoric, and evernic acid.

Orchil, or archil, occurs in commerce in two forms—paste and liquor. It was formerly made by treating the lichens with putrid urine, and, at a subsequent stage, with slaked lime. The process usually adopted in England is as follows:—The weed, preferably the *Roccella tinctoria*, is picked, and torn or cut into small fragments, and put into iron drums provided with stirrers and mixed with a dilute solution of ammonia. The temperature of the mass is kept at from 35° to 45° C. for a period ranging from 5 to 6 days. A fermentation soon commences, which must be carefully watched and should not be allowed to go on for too long a time; otherwise the colouring matter is destroyed, with the formation of a dirty brown substance. Samples are taken out from time to time and dye-tests made, in order to observe the stage of the operation. When the colouring matter ceases to increase the fermentation is stopped. The product is archil paste. In making orchil liquor, the weed is treated with water containing ammonia, and the fibrous matter, which is practically worthless, removed. The liquid, which contains the colour-giving principles, is then submitted to fermentation, as above described. M. Freson,*

* Crace Calvert, *Dyeing and Calico Printing*, p. 230.

a large manufacturer of orchil in France, has devised the following method:—After separating earthy impurities, the lichens are ground up with water between mill stones into a pulp. This pulp is then carefully washed with cold water and thrown on to a coarse filter made of loosely-woven woollen cloth. The turbid liquid contains nearly the whole of the colour-giving principles, while the washed pulp on the filter consists almost entirely of woody fibre. A small quantity of stannic chloride is added to the liquor by which the colour-yielding principles are coagulated and precipitated. The precipitate is collected and quickly washed and brought into troughs, with the requisite amount of ammonia, where it is left, with occasional stirring, for about a month.

An orchil preparation, sold under the name of French purple, is made by M. Marnas, of Lyons.* It is said to yield faster shades than the ordinary orchil. The lichens are treated with a dilute solution of ammonia, and the resulting liquid acidulated with hydrochloric acid, which precipitates the colour-giving principles. The precipitate is collected, well washed with water, and dissolved in strong ammonia. The solution thus obtained is kept for a period of 20 to 25 days at a temperature ranging from 70° to 75° C. A magnificent purple colour is developed, which is precipitated by the addition of calcium chloride as a purple lake. In order to dye silk or wool with French purple it is mixed with its own weight of oxalic acid and boiled up with water.

Cudbear, which comes into the market in the form of a dark brownish-red or purple powder, is prepared, in the first instance, in the same way as orchil paste. The weed usually selected for cudbear is the *Lecanora tartarea*. When the fermentation is complete the mass is dried and ground.

A solution of cudbear or orchil gives the following reactions:—

Acids,	Solution yellow.
Alkalies,	„ bluer.
Lead acetate,	Deep crimson precipitate.
Calcium chloride,	Red precipitate in strong solutions.
Stannous chloride,	At first redder, then yellow.
Alum,	Solution redder.
Basic alum,	Crimson-red precipitate.

Orcëin is the principal colouring matter of archil and cudbear. It is produced by the action of ammonia and oxygen on orcinol or orcin, $C_6H_3(C_6H_3)(OH)_2$. According to Liebermann, two compounds may be produced, depending upon the amount of ammonia used. The composition of the two bodies is given as $C_{14}H_{11}NO_3$ and $C_{14}H_{12}N_2O_3$ respectively.*

Dyeing.—Since the introduction of many of the azo-dyes and the application of alizarin colours to *wool*, the amount of orchil and cudbear used in dyeing has been gradually though slowly declining. Nevertheless

* Crace Calvert, *Dyeing and Calico Printing*, p. 231.

large quantities of these colouring matters are still used, and, although fugitive, on account of certain characteristics, they seem difficult to replace. Great quantities are used for "bottoming" indigo. Cudbear and orchil are used in conjunction with other dyestuffs for producing compound shades, such as browns, maroons, and clarets, on wool and silk. A considerable amount is used in the dyeing of carpet yarn. The colouring matter is substantive, requiring no mordant, and possesses the useful property of dyeing in a neutral, acid or slightly alkaline bath. It does not rush on to the fibre, but dyes slowly, regularly, and evenly. In deep shades the colour has an intensity and body which cannot be well equalled by any of the numerous coal-tar substitutes. Cudbear and orchil dye best in a neutral bath, producing a bluish-red or dull magenta shade; but they are frequently applied with sulphuric acid in conjunction with extract of indigo and other "acid" colours. An acid bath turns the shade redder and brighter.

About 3 per cent. of sulphuric acid is a convenient amount to use. Frequently alum and tartar are used in place of sulphuric acid. The colour is not fast to light nor milling; but resists soaping fairly well, becoming bluer.

Silk is dyed in a bath containing soap solution with, or without, the addition of acetic acid.

Cudbear and orchil are not applicable to cotton.

Detection on the Fibre.—The ash will probably contain either no mordant or a little alumina. Chromium may be present, especially if logwood, fustic, or similar colouring matter has been used in dyeing the shade. The following reactions are given by the pure colouring matter:—

Hydrochloric acid, .	Solution and fibre red.
Sulphuric acid, .	Fibre and solution purple; on dilution, solution red and fibre almost colourless.
Caustic soda, . .	Fibre and solution bluish-purple, colour slowly removed.
Ammonia, . . .	As with caustic soda.
Nitric acid, . .	Yellow.
Stannous chloride, hydrochloric acid, and water,	Decolorised.
Boiling alcohol, .	Bluish-red solution.
Boiling carbonate of soda ($\frac{1}{2}$ per cent.), .	Violet solution.
Boiling 5 per cent. solution of sulphuric acid, .	Orange solution, turned violet by soda.

In a compound shade, in the presence of indigo, logwood, fustic, alizarin, &c., it is best detected by boiling with alcohol, adding water to the alcoholic extract, and evaporating to a small bulk with a few threads of worsted yarn. The yarn is then dried and carefully tested as above. Orchil and cudbear are thus readily distinguished from magenta by the action of hydrochloric acid and caustic soda respectively, magenta being decolorised by both reagents.

COCHINEAL, KERMES, AND LAC-DYE.

These colouring matters are all derived from the animal kingdom.

Cochineal is the female of the *Coccus cacti*, an insect which lives and propagates on certain kinds of cactus, especially the *Nopal* or *Cactus opuntia*. The plant and insect are natives of Mexico and Guatemala, but have been successfully introduced into the Canary Islands, as well as Algeria, Java, and Australia. The production, however, is almost confined to Guatemala and the Canaries. The male insect is much smaller than the female, and is furnished with wings. It does not yield a dye. The female has no wings, and remains attached to one spot on the plant. At the age of about three months the female insects are swept from the leaves into small straw baskets, and are either killed by being thrown into hot water, and afterwards dried in the sun or in stoves; or they are placed in a bag and stoved at once. The latter method yields the silver cochineal, so called on account of the peculiar white lustrous appearance which the product possesses. When the insect is first thrown into water it forms the black cochineal. The weight of the dried insect is about $\frac{1}{10}$ grain, so that 70,000 are required to produce 1 lb. of cochineal. An acre of the cactus yields 250 to 300 lbs. If treated with warm water for some hours the dried insect swells and takes a hemispherical shape, when its structure can be seen.

The colouring principle of cochineal is *carminic acid*, $C_{17}H_{18}O_{10}$. Schutzenberger prepares it in the following manner. The cochineal is ground and extracted with ether in order to remove fatty matters, &c. It is then treated with hot water, and the solution filtered. The solution contains the colouring matter as well as many impurities. Acetate of lead and a little acetic acid are added, which cause a precipitate of lead carminate mixed with a little lead phosphate. The precipitate is well washed and suspended in water, and decomposed with an insufficient quantity of sulphuric acid, in order to leave the lead phosphate intact. The liquid is filtered hot, and the solution evaporated at about 50° C. The residue is treated with absolute alcohol, and the solution, on evaporation and cooling, yields carminic acid in a crystallised state. Carminic acid is a purple body soluble in water, alcohol, carbon bisulphide, and benzene. It dissolves in strong sulphuric acid and hydrochloric acid without decomposition. Nascent hydrogen decolorises it, but it again becomes red on exposure to the air. On boiling carminic acid with dilute sulphuric acid, it splits up into a sugar and carmine-red, a purple-red substance which appears green by reflected light. Liebermann,* however, could obtain no confirmation of the statement that the colouring matter is a glucoside.

The aqueous solution of carminic acid is not changed by exposure

* *Journ. Soc. Chem. Ind.*, 1885, p. 585.

to the air. It dissolves in caustic alkalies with a beautiful purple colour. Its solution gives purple precipitates with baryta and lime water, barium chloride, and acetates of lead and copper; red precipitate with stannic chloride; orange-red precipitate with potassium tartrate or oxalate. Alumina removes the whole of the colouring matter from an aqueous solution, yielding a beautiful red lake, which on being heated becomes purple.

On account of the presence of phosphates and tyrosine, a decoction of cochineal behaves somewhat differently to a solution of carminic acid. The following reactions take place with a decoction of cochineal:—

Acids,	Yellow-red colour.
Alkalies,	Violet colouration.
Lime water,	Violet precipitate.
Alum,	Slowly forms red precipitate.
Aluminium chloride,	Reddish-violet precipitate.
Stannous chloride,	Violet precipitate.
Stannic chloride,	Bright scarlet colouration.
Ferrous sulphate,	Violet-grey precipitate.
Copper sulphate,	Violet precipitate.
Lead acetate,	„ „
Zinc sulphate,	„ „
Oxalic acid,	Red „

Since the introduction of the azo-scarlets, the amount of cochineal used in dyeing has decreased considerably; nevertheless, large quantities are still used in dyeing woollen cloth, and, to a lesser extent, worsted yarn and slubbing. The scarlet cloth for the English army is all dyed with cochineal. Formerly a considerable amount of cochineal was used in silk dyeing, but at the present day it has been almost entirely superseded by the coal-tar colours. In cotton dyeing cochineal finds little or no application; small quantities are used in the printing of pinks.

In the dyeing of wool, two distinct red shades are obtained by cochineal, viz., a crimson and a scarlet. The latter is of the greater importance, and is obtained by tin mordants. The dyeing and mordanting is done in one bath. A cochineal scarlet is faster to light than an azo-scarlet. On being scoured or milled it does not lose much colour, but becomes duller and bluer. An azo-scarlet, on the other hand, becomes yellower. A cochineal scarlet does not bleed and stain the neighbouring fibres like the azo-scarlet.

Cochineal gives the following series of shades with the various mordants:—

Chromium mordants,	Purple.
Aluminium „	Crimson.
Iron „	Purple.
Copper „	Claret.
Tin „	Scarlet.

Tin and alum salts are the only useful mordants.

Dyeing of Wool.—In dyeing scarlets and oranges with cochineal, the mordanting and dyeing may take place in separate baths or in one bath. The latter is the usual method adopted in practice. When separate baths are used, 4 to 6 per cent. of stannous chloride and a similar quantity of tartar are taken, and the wool entered at about 60° C. The bath is gradually raised to the boil, and kept at or near the boiling point for from three-quarters to one hour. The material is either washed or taken direct to the second bath (containing 10 to 20 per cent. of ground cochineal) and dyed one to one and a half hours. The shade obtained is a bluish-scarlet. In the one-bath system there are numerous modifications of cochineal-scarlet dyeing. Some dyers use stannous chloride (tin crystals); others tin spirits of various kinds, such as scarlet spirits or nitrate of tin, muriate of tin, sulpho-muriate, &c. The simple chloride of tin, which consists merely of stannous chloride and hydrochloric acid, is, as a rule, to be preferred to the tin crystals, since the free hydrochloric acid, when not present in too great an excess, acts beneficially. The lake formed by the tin salt and the colouring matter of cochineal is kept longer in solution and the colour penetrates to the centre of the cloth, whereas, in the case of hard woollen goods, in the absence of free hydrochloric acid, the colour would be more or less deposited on the surface. Again, in the case of calcareous or alkaline waters, the hydrochloric acid prevents a precipitation and consequent loss of mordant. For 100 lbs. of wool, the dye-bath may be prepared by adding 5 to 6 lbs. of oxalic acid, 4 to 5 lbs. of stannous chloride (or its equivalent of tin spirits), and 10 to 20 lbs. of cochineal. Instead of oxalic acid, tartar or argol, or a mixture of oxalic acid and tartar, may be used. The oxalic acid or tartar should be added to the bath before the stannous chloride, otherwise a precipitation of stannous oxychloride occurs, which not only causes a loss of mordant, but may produce stains. If, however, a solution of stannous chloride containing sufficient hydrochloric acid be used, this precipitation does not take place. After boiling the mixture of dye and mordant for about ten minutes, cold water is added to the bath, and the goods entered at a temperature of about 70° C. The bath is gradually raised to the boiling point, during the course of three-quarters of an hour, and boiled for three-quarters of an hour longer. A deficiency of tin gives a dull bluish shade, while an excess produces a paler scarlet. Tartar increases this intensity, and an excess gives a yellower shade of scarlet. As a rule a small proportion of yellow colouring matter is used in scarlet dyeing, the substances used being weld, flavin, fustic, or Persian berries. For orange shades, of course, larger proportions of yellow and only a small percentage of cochineal are taken. The one-bath system produces yellower and more brilliant shades than when separate baths are used for mordanting and dyeing. More cochineal is required to give a certain shade by the single-bath than by the two-bath method, since in the former case much of the

colouring matter remains in the bath (after dyeing) in combination with the mordant. For successive lots of material to be dyed, however, smaller quantities of cochineal suffice.

In dyeing with cochineal the vats employed should be either of wood or stone. In the presence of iron or copper the shades obtained are liable to be dull, since if traces of these metals dissolve they form with cochineal dark violet or purple lakes. If much hydrochloric acid is used the scarlet is not greatly affected by small quantities of iron or copper.

Cochineal crimson is obtained by means of aluminium mordants, and, like the scarlet, may be dyed in either one bath or two. If separate baths are used, the wool is mordanted with 6 per cent. of alum and 6 per cent. of tartar, and dyed in a fresh bath with 15 to 20 per cent. of cochineal. The same proportions may also be used for the single bath method, or oxalic acid may be taken instead of tartar. A bluer shade of crimson is obtained by adding a little alkali to the bath—ammonia or sodium carbonate. The shade may also be modified by adding orchil, cudbear, or ammoniacal cochineal.

Ammoniacal cochineal is obtained by allowing a mixture of ground cochineal and ammonia to remain in contact for some days. The proportions used are one part of cochineal and three parts of ammonia. A chemical change occurs, resulting in the formation of carminamide from carminic acid—



When the change is complete the mixture is heated in order to drive off the excess of ammonia. In some cases about 40 per cent. of hydrated alumina is added, and the whole of the ammonia driven off by heat. The mass is afterwards moulded into cakes. Ammoniacal cochineal is used for dyeing wool purple and crimson, and in conjunction with ordinary cochineal for rose reds. The crimsons are not so readily affected by acids as those given by ordinary cochineal. Ammoniacal cochineal gives a beautiful purple precipitate with oxychloride of tin; cochineal direct gives, as previously stated, a scarlet precipitate. The mordant which works best with ammoniacal cochineal is the nitrate of tin.

Rose pink is obtained on wool by dyeing in a vat containing the following ingredients (for 100 lbs.):—2 lbs. of ammoniacal cochineal paste, 2 lbs. of ground cochineal, 1 lb. of tin dissolved in 8 lbs. of nitric acid, and 4 lbs. of tartar.

Detection on the Fibre.—The mordant on wool dyed with cochineal will be found to be either tin or alum. The following reactions are given by this colouring matter on wool, mordanted with alum and tin salts respectively:—

Reagent.	Tin Mordant.	Alum Mordant.
Hydrochloric acid, . . .	Orange-red.	Scarlet.
Sulphuric acid, . . .	Dark violet.	"
Nitric acid, . . .	Yellow.	Yellow.
Stannous chloride, hydrochloric acid and water, . .	Orange.	Orange-red.
Caustic soda,	Red-violet.	Red-violet.
Ammonia,	"	"
Boiling alcohol, . . .	<i>Nil.</i>	<i>Nil.</i>

Cochineal, on the fibre, is distinguished from azo-scarlets by the action of caustic soda; the azo-scarlets being either partially decolorised or turned orange, cochineal becoming purple. Boiling weak acids turn cochineal-scarlet yellower and the solution is reddish-orange, which, on addition of caustic soda, becomes purple. An azo-scarlet is less affected by acids, the solution is a pale bluish-pink, which is either decolorised or becomes yellow-orange on addition of caustic soda. Boiled with a weak solution of soap, cochineal becomes bluish-crimson, azo-scarlets yellower and much lighter. From alizarin, cochineal is distinguished by the action of weak and strong hydrochloric acid, cochineal being little affected, whereas alizarin becomes yellow. The acid solution in both cases becomes purple or violet on addition of an alkali.

Kermes consists of the dried insect known as the *Coccus illicis*, which lives on a species of oak, the *Quercus coccifera*. The insects are collected in the month of June, and killed by being exposed to the vapours of acetic acid evolved by heating vinegar. They are afterwards dried, and are then ready for use. Kermes is but little, if at all, used in England; but in South France, Spain, Morocco, and Turkey it is still used for dyeing leather and woollens. Kermes was known to the ancients, and has been used in the East as a dye from time immemorial. The colouring principle of kermes is identical with, or very closely related to, the carminic acid of cochineal. On account of minute quantities of other substances being present, it does not dye such bright shades as cochineal; but the colours are not so readily affected by alkalies, soap, or perspiration as cochineal colours are. Kermes of good quality has a deep red colour, and possesses a somewhat pleasant odour. The colouring matter is soluble in water, and its solution is turned brown by acids and violet or crimson by alkalies. With the various mordants it dyes similar shades to those given by cochineal, though not so bright. The tinctorial power of kermes is little, since it requires twelve times as much kermes as cochineal to produce a given shade of claret or crimson. Kermes, as well as cochineal, was formerly supposed to consist of little berries or grains, and the colours dyed with them were said to be grained or ingrained. The term "grain colours"

is still used at the present day, signifying shades dyed with cochineal. The term "ingrain colours" has recently been applied to shades obtained from primuline.

Lac-dye is the product of a small insect, the *Coccus lacca*. It is a secondary product in the manufacture of shellac. The insect lives on the twigs of trees of the genus *Ficus*, especially the *Ficus religiosa* or banyan tree, which grows in Bengal, British Burmah, Assam, and other eastern countries. The insects reproduce and multiply with such rapidity that in a short time they entirely cover the surface of the twigs to a thickness of a quarter of an inch, and adhere very firmly to the wood. The natives break off these twigs just before the time of hatching, and expose them to the sun to kill the insect. The product is stick-lac. It contains about 10 per cent. of colouring matter and 70 per cent. of resin. The stick-lac is ground and triturated for some hours with water, or, according to some authorities, with a weak alkali. The colouring matter dissolves and is precipitated by adding a solution of alum. The deposit is collected and placed on a canvas filter or strainer, and afterwards pressed so as to form cakes about $2\frac{1}{2}$ inches square and from $\frac{1}{2}$ inch to $\frac{3}{4}$ inch thick. The exact mode of preparation, however, is kept secret.

After treating stick-lac with water, the residue, when dried, constitutes seed-lac. When seed-lac is melted and filtered through cotton it forms shellac.

Lac-dye has been manufactured and used in India for centuries. It was first imported into England in 1796 and at one time was used to a very much greater extent than at present. It produces a colour similar to cochineal but fuller, although not so brilliant. It is faster than cochineal. This was formerly considered to be due to the presence of resinous matters in lac, but it is more probably a property of the colouring matter itself; since recent investigations have shown that, although similar to carminic acid, the colouring matter of lac is a distinct body and has been named by Schmidt *laccainic acid*.

Laccainic acid forms a brownish-red crystalline powder which melts at 180° . It is soluble in alcohol, wood spirit, and glacial acetic acid. The following analyses of lac-dye are given by R. E. Schmidt* :—

	1.	2.
Water,	9.0	11.26
Colouring matter,	10.4	13.20
Other organic matter,	64.9	57.30
Mineral matter,	15.7	18.24

A parcel of six samples examined by Rawson gave on analysis the following figures :—

	1.	2.	3.	4.	5.	6.
Water,	11.20	10.60	9.60	8.04	10.50	6.30
Colouring matter,	18.33	13.74	13.37	8.24	16.50	3.66
Other organic matter,	55.47	55.91	65.47	66.32	58.74	66.54
Mineral matter,	15.00	19.75	11.56	17.40	14.26	23.50

* *Journ. Soc. Dyers and Col.*, 1887, p. 122.

The amount of colouring matter was obtained by the following process:—1 gramme of finely-powdered lac was boiled with hydrochloric acid, the solution diluted largely with water and an excess of acetate of lead added. The precipitate was collected on a filter and thoroughly washed, and then suspended in water, whilst a current of sulphuretted hydrogen was passed through the liquid. After filtering from the lead sulphide thus formed, the clear solution was evaporated to dryness and extracted with absolute alcohol. The alcoholic solution was then evaporated to dryness and weighed.

Lac is used for dyeing wool scarlet, orange, and crimson shades. The colouring matter is only sparingly soluble in water, on account of the presence of so much resinous and mineral matter in commercial lac. Before use, the lac is ground up with the requisite amount of tin spirit, and usually a little hydrochloric acid, and allowed to stand about a day. It is then added to the bath, and the goods are dyed in exactly the same manner as with cochineal, adding either oxalic acid, tartar, or both. In practice, it is often found advantageous to combine the brightness of cochineal with the solidity and permanency of lac dye. Consequently, lac and cochineal are frequently used together; or, after dyeing the wool with lac, it is taken to a fresh bath containing cochineal. A good fast scarlet is produced upon cloth (100 lbs.), by dyeing in a vat containing the following ingredients:—8 lbs. of lac (previously ground up with part of the tin spirits), 5 lbs. of cochineal, 5 lbs. of tartar, 20 lbs. of tin spirit (44° Tw.) and flavin, $\frac{1}{2}$ oz.

CATECHU OR CUTCH AND GAMBIE

These dyestuffs are obtained from various species of *Acacia*, *Areca*, and *Uncaria* growing in India. They closely resemble each other in their properties, and, for some time, there was much doubt regarding their origin. Catechu or cutch, also known as *terra japonica*, is obtained from the softer part of the wood, and from the pods of the *Acacia catechu*; and also from the betel or areca nut, which is the fruit of the palm tree, known as *Areca catechu*. The wood or nuts are boiled in water, and the solution obtained evaporated to a syrup, when it is spread on the ground, and on cooling solidifies.

Catechu has been used in the East from time immemorial for the purposes of dyeing and tanning, and also in medicine.

The two principal varieties of cutch or catechu are known respectively as Bombay and Bengal catechu.

Bombay catechu, the product of *Areca catechu*, is considered to be the best. It is imported in dense irregular lumps of a dark brown colour, weighing about a hundredweight. It dissolves in boiling water with a deep brown colour, and the solution gives copious precipitates with gelatin and sulphuric acid.

Bengal catechu is the product of the *Acacia catechu*. It is of a pale brown colour, and contains less tannin, but more catechin, than the Bombay variety.

Gambier is obtained by extracting the leaves of the *Uncaria gambier*, a shrub growing abundantly in India and the Malacca Islands. Gambier occurs in commerce in blocks and in small cubical pieces. It is opaque and of a brownish-yellow colour. It is only slightly soluble in cold water, but almost completely soluble in boiling water. Its colouring matter is in a less oxidised state than that of cutch.

Catechu or cutch and gambier contain varying amounts of a tannin, known as catechutannic acid or mimotannic acid, and a white crystalline body called catechin or catechuic acid. There is also present a brown amorphous body, produced by the oxidation of the catechin and catechutannic acid during the process of extraction and evaporation.

Catechutannic acid may be prepared by boiling powdered catechu with a small quantity of water, and allowing the mixture to stand some days in order that the catechin may separate. The solution is filtered and evaporated to dryness. The residue is dissolved in alcohol and the solution treated with ether, and, after again filtering, evaporated to dryness. It may be further purified by treatment with water and ether. Catechutannic acid is readily soluble in water and alcohol, but insoluble in ether. Its aqueous solution gives precipitates with gelatin and with tartar emetic; with ferric acetate it gives a green precipitate. On exposure to air the aqueous solution is gradually oxidised, becoming red. The change takes place very rapidly in the presence of alkalis.

Catechin or catechuic acid may be obtained from the residue after treating catechu with cold water. It is dissolved in a small quantity of boiling water and precipitated by lead acetate and acetic acid. The precipitate is washed, suspended in water, and decomposed by sulphuretted hydrogen. The filtrate is then carefully evaporated to a small bulk and allowed to crystallise. Catechin may also be extracted from finely-powdered catechu by means of dry ether, in which liquid catechutannic acid is insoluble. Catechin is a white, silky, crystalline body, sparingly soluble in cold water, but freely soluble in boiling water and in alcohol and ether. The aqueous solution gives a green colouration with ferric chloride, but produces no precipitate with gelatin. An alkaline solution of catechin rapidly absorbs oxygen from the air with the formation of a brown substance known as japonic acid. It is said to be this compound which constitutes the brown colour of goods dyed with catechu. Catechu and gambier possess an astringent taste with a sweet after-flavour. A solution gives the following reactions:—

Gelatin,	Copious reddish precipitate.
Alkalies,	Brownish hue.
Alum,	Yellowish colour; solution clearer.
Ferrous sulphate,	Olive-green colouration.
Ferric sulphate,	Dark green colouration.
Copper sulphate,	Olive colouration.

Acetate of copper,	Blackish-brown precipitate.
Lead acetate,	Yellowish-grey precipitate.
Potassium bichromate,	Abundant brown precipitate.

A colouring matter, known in the trade as *prepared cutch* or *patent cutch*, is made from gambier. There are various modes of preparation, some of which are kept rigidly secret. According to one process, the gambier is melted with the addition of about 1 per cent. of bichromate of potash and then poured into wooden frames to solidify. The catechin is thereby oxidised into brown resinous bodies, probably japonic acid and similar compounds. The product dyes much redder shades than the original gambier. In place of bichromate of potash, copper sulphate and alum are sometimes used in the preparation. These substances may be detected in the ash after igniting the sample.

Application.—Catechu and gambier are used largely in cotton dyeing, also in calico printing and in silk dyeing. In the dyeing of wool, these substances find only a limited application, although they might in many cases be used with advantage. Both the catechutannic acid and the catechin are utilised in dyeing. The former gives olives and brown olives with mordants, and the latter browns of various shades.

Dyeing of Cotton.—There are various modifications of applying catechu and gambier to the textile fibres, and, broadly speaking, the same methods may be used for both wool and cotton. The usual method consists in boiling the cotton with a solution of catechu or gambier with an addition of copper sulphate or copper acetate, in the proportion of one part of copper salt to ten parts of colouring matter. After allowing to stand some hours, the cotton is worked for about half an hour in a fresh bath (hot) containing 2 per cent. of bichromate of potash, washed and dried.

According to the manner in which the dye has been prepared, samples of catechu and gambier behave very differently in the dye-bath. The shade produced by some varieties undergoes but little change when passed into the "bichrome" bath, whilst that of others is developed and intensified greatly. Gambier as a rule develops much more than catechu. If the copper salt is omitted, as it is by some dyers, a greater development takes place in the "bichrome" bath. Copper salts render the shades much faster to light and should always be used in dyeing with catechu. The shades are also considerably deeper. In some cases the copper salt is applied in a separate bath; but the more general plan consists in mixing it with the catechu or cutch, as above stated. The treatment with bichromate of potash is supposed to oxidise the catechutannic acid and catechin to japonic acid, which, being insoluble, is thus firmly fixed on the fibre.

Catechu and gambier are largely used in dyeing compound shades in conjunction with logwood, fustic, red woods, &c.

The basic coal-tar colours, such as Bismarck-brown, magenta,

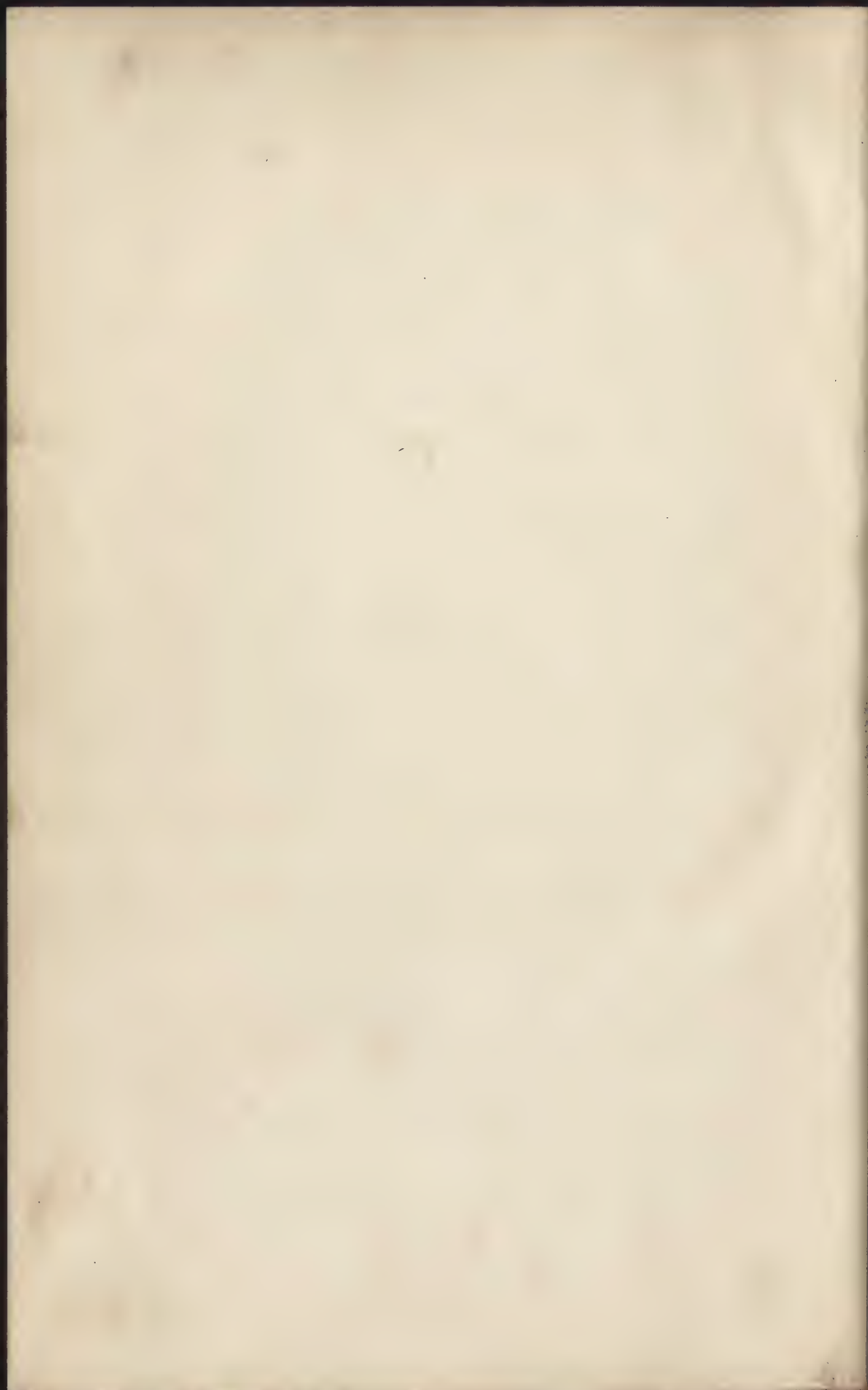
auramine, &c., are also frequently employed. The catechutannic acid acts as the mordant for the artificial colouring matter.

Dyeing of Wool.—As already stated, wool may be dyed in the same manner as cotton. Or the wool may be simply boiled in a solution of catechu, and worked in a fresh bath with about 2 per cent. of copper sulphate, ferrous sulphate, or potassium bichromate; the method being essentially the same as that usually employed for camwood-browns. From 2 to 5 per cent. give light brown or drab shades; 10 to 20 per cent. good rich browns, which may be modified by the addition of logwood, fustic, &c. In some cases the wool is mordanted with $\frac{1}{2}$ to 1 per cent. of bichrome before dyeing as well as “saddened” or fixed afterwards in the same manner as fast logwood blacks. Wool dyed with catechu is very fast to milling and scouring and fairly fast to light. If used in large proportions, catechu, however, like other astringents (sumach, myrabolans, &c.), is apt to give the wool a harsh feel; but this property appears to have been exaggerated, and, no doubt, the dyestuff would be found highly advantageous in place of many other dyes at present used. For wool dyeing, if this harshness is found to be a serious obstacle, the cutch should be ground up with cold water, and, after running off the liquor, the residue, consisting mainly of catechin, alone used.

Dyeing of Silk.—Gambier is largely used in black-silk dyeing, principally for the purpose of weighting. The silk is first steeped in basic ferric sulphate, and then in yellow prussiate of potash and hydrochloric acid, which thus produces Prussian blue on the fibre. It is then worked in a bath containing about 200 per cent. (for heavy weighting) of gambier; after half an hour 10 per cent. of stannous chloride is added, and the silk is again entered and worked one to two hours. In some cases the addition of stannous chloride is omitted. (See *Black Dyeing of Silk* under *Logwood*, pp. 358-360.)

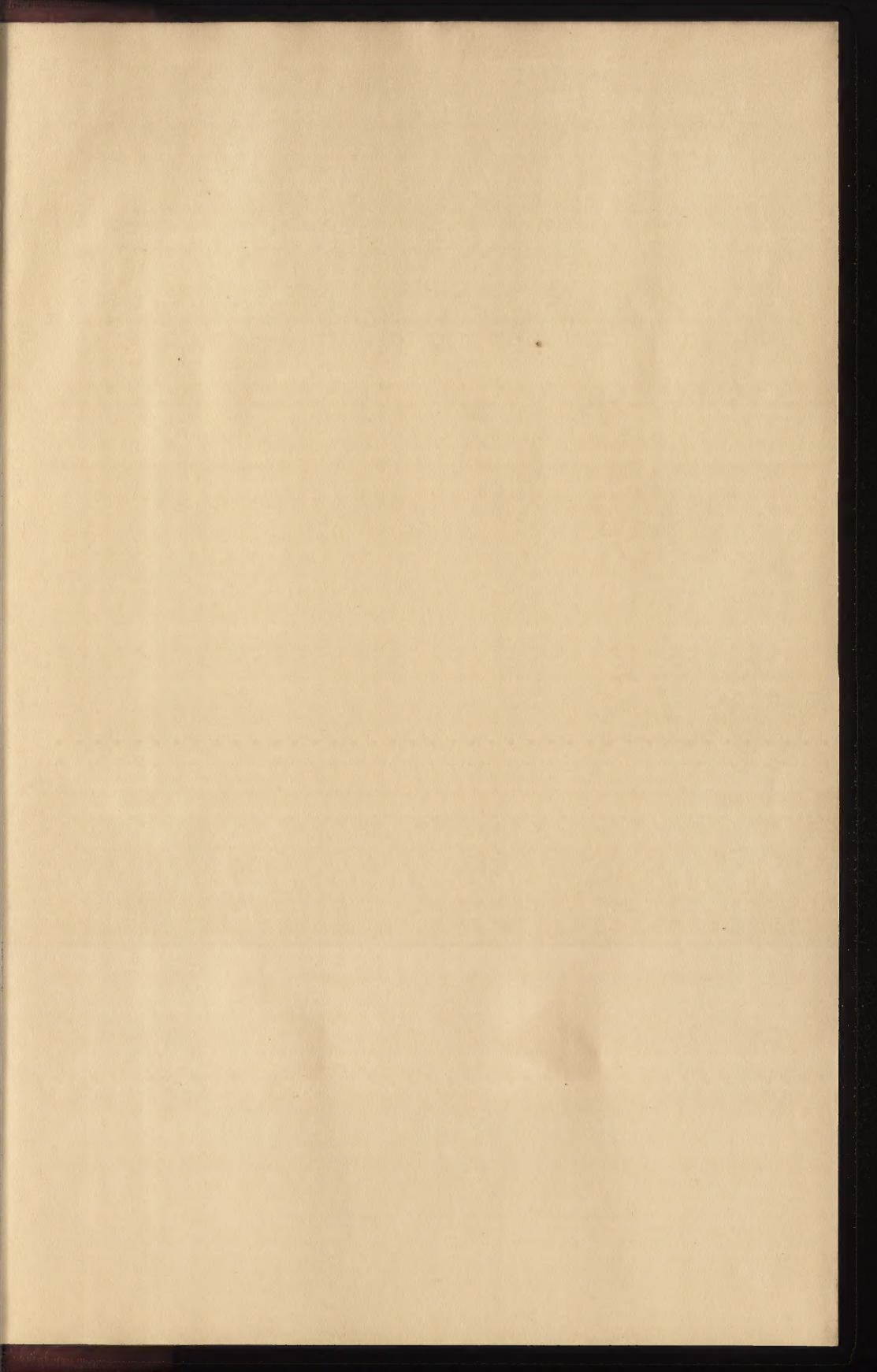
Detection on the Fibre.—Catechu is not often met with on wool, but either upon wool or cotton the ash will usually be found to contain oxide of chromium and frequently copper oxide. The colouring matter is little affected by reagents. The following are its chief characteristics on the fibre:—

Sulphuric acid,	Little change; brownish solution.
Hydrochloric acid,	Rather yellower: faint yellow solution.
Nitric acid,	Orange.
Caustic soda (10 per cent.), .	Redder.
Boiling 5 per cent. solution of sulphuric acid,	Fibre yellower; solution light yellow-brown; red-brown on addition of soda.
Boiling $\frac{1}{2}$ per cent. solution of sodium carbonate,	
	<i>Nil.</i>









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